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Information from
Health Impacts of Polynuclear
Aromatic Hydrocarbons

CHARACTERISTICS OF PNA
IN THE ENVIRONMENT

The information in this chapter is based on:

*Environmental, Health and Control Aspects of Coal Conversion:
Volume 2, An Information Overview*, ORNL/EIS-95, April 1977,
prepared by H.M. Braunstein, E.D. Copenhaver and H.A. Pfuderer
of Oak Ridge National Laboratory for Energy Research and De-
velopment under Contract W 7405-eng-26.

*Critical Pathways of Polycyclic Aromatic Hydrocarbons in
Aquatic Environments*, NTIS CONF-790486-3, 1979, prepared
by S.E. Herbes, G.R. Southworth, D.L. Shaeffer, W.H. Griest
and M.P. Maskarinec of Oak Ridge National Laboratory.

Most of the current information concerning polycyclic aromatic hydrocarbons
(PAH) has been generated not from coal conversion processes, but from related
technologies. However, as coal conversion pilot plants continue to operate and
full-scale plants are built, the literature should begin to address more of the en-
vironmental aspects of coal conversion, such as the effects of associated effluents
For example, Herbes, Southworth, and Gehrs (1) have compiled an extensive
critical literature review of the environmental hazards of anticipated organic com
ponents of aqueous coal liquefaction products, presented at the recent Trace Sub
stances in Environmental Health Conference (University of Missouri 1976).

The environmental role of PAH is of particular concern because some PAH are
potential health hazards. PAH are found in small but detectable concentrations
in air, water, and soil samples of all types. The concentrations found are typ
ically small, ranging from 0.001 to 10 $\mu g/\ell$, but they accumulate in organic fatt,
material and can thus concentrate in the food chain (2).

BACKGROUND CONCENTRATIONS

Not all PAH are the result of man's activities. Biosynthesis of PAH by plants
and microorganisms is well known; the National Academy of Sciences (3) em-

phasizes the importance of examining the possible contribution of vegetation to the total carcinogenic burden in the environment.

Andelman and Suess (4) cite the research of Gräf and Diehl (5) and Gräf and Nowak (6) on the synthesis and physiological functions of PAH in plants. Wheat and rye seeds containing only a trace of PAH were grown in PAH-free solutions in both the presence and absence of light. Five- to ten-day-old seedlings contained 10 to 20 μg of benzpyrene (BP) per kilogram of dried material; BP was the only PAH analyzed for in the experiments. The researchers conclude that BP is synthesized by the plants in both the presence and absence of light and thus that PAH likely are synthesized worldwide and have always existed in man's environment. Andelman and Suess agree that the evidence indicates that PAH and other hydrocarbons are naturally ubiquitous. However, Grimmer and Duvel (7) were unable to detect PAH in higher plants grown in PAH-free environments.

A planktonic member of the plant kingdom, the alga *Chlorella vulgaris*, is known to synthesize several PAH (8); algal extractions contained 10 to 50 μg per kg of PAH (9). Phytoplankton play an important role in the annual production of hydrocarbons (cycloparaffin and aromatic); Smith (10) calculates a production rate of 13 tons (87 bbl) of hydrocarbons per square mile of ocean surface. Smith used a planktonic hydrocarbon content of 2,000 ppm of the dry weight (furnished by an analysis of phytoplankton by B.H. Ketchum of the Woods Hole Oceanographic Laboratory) and a value of 6,400 tons per square mile of ocean surface for the annual production rate of phytoplankton to determine the annual hydrocarbon output by oceanic phytoplankton.

Blumer (11) studied the BP content of rural soils in Massachusetts and Connecticut (Table 3.1). It was suggested that the BP in these soils is indigenous because the rural areas sampled are distant from major highways and industries. The natural sources are thought to be pyrolytic decomposition of wood, transformation of plant organic matter to peat and lignite, and activity of soil microorganisms. These studies prompted Blumer to postulate, as did Gräf and coworkers, that hydrocarbons, including carcinogenic species, have been in the environment throughout man's entire history.

Andelman and Suess (4) report the synthesis of BP by soil bacteria in citing the research of Knorr and Schenk (12). Laboratory-cultured bacteria synthesized and accumulated BP in amounts of 2 to 6 μg per kilogram of dried material. Suess (13) reports the existence of bacterially produced carcinogenic PAH in the upper layers of the earth in concentrations of 100 to 1,000 μg/kg; these PAH leach through the soil, giving groundwater PAH concentrations of 0.001 to 0.010 μg/ℓ in the absence of anthropogenic sources.

Mallet (14) studied old sediments and found 19.5 μg/kg of benzo[a] pyrene (BaP) in a fragment from a 50-m depth. It was concluded that this hydrocarbon could be formed from phytoplanktonic lipids under the influence of anaerobic bacteria, particularly *Clostridium putride*. Mallet and Tissier (15) further investigated the biosynthesis of BP by bacteria in a series of laboratory experiments using *C. putride* and *Escherichia coli*. The initial experiment used humus from a forest soil near an industrial area. This soil was sterilized, analyzed for BP, inoculated with *C. putride*, and stored for 4 months at laboratory temperature. The initial concentration, 80 to 100 μg of BP per 100 g of soil, increased to 160 μg at the end of 4 months. A second experiment involved forest soils extracted from rural

areas having an initial BP concentration of 1 to 2 μg per 100 μg of soil. One batch of this rural soil was ground, sterilized dry at 170°C, and incubated for 6 months anaerobically after inoculation with C. putride. The same experiment was also performed with E. coli. Table 3.2 shows that, after 6 months, about 4 μg of BaP was detected in soils containing both C. putride and E. coli. In another experiment, Mallet and Tissier (15) extracted from the soils what they believe to be the active substances for the formation of BaP, namely, fatty acids, and added them to soft agar inoculated with C. putride. After 4 months of incubation at 31°C, no trace of BaP was detected in the control tubes; however, significant but small amounts of the hydrocarbon were found in the samples inoculated with the C. putride.

Table 3.1: BaP in Soils

Origin and Type of Soil	Concentration (μg/kg)
Oak forest, West Falmouth, Cape Cod, Mass.	40
Pine forest, West Falmouth, Cape Cod, Mass.	40
Mixed forest, West Falmouth, Cape Cod, Mass.	1,300
Mixed forest, eastern Conn.	240
Garden soil, West Falmouth, Cape Cod, Mass.	90
Plowed field, eastern Conn.	900

Source: Reference (11) as cited in ORNL/EIS-95

Table 3.2: Soil Sterilized in the Pasteur Oven at 170°C

BP Without Addition of Bacteria (μg)	Bacteria Added	BP After Experiment (μg/100 g)
Possible traces	Clostridium putride	2.6
Traces	Clostridium putride	4.2
1.40	Clostridium putride	3.95
Traces	Clostridium putride	1.95
2	Clostridium putride	2.6
0.75	Escherichia coli	2.25
Traces	Escherichia coli	2.20
1	Escherichia coli	4.75
	Escherichia coli	5.1
	Escherichia coli	5

Source: Reference (15) as cited in ORNL/EIS-95

These investigations corroborate the results observed in marine muds, where the amounts of BP are generally considerable; BP is capable of being synthesized by anaerobic microorganisms or reduced by certain aerobic bacteria of the Bacillus type (15).

Other papers by Mallet et al (16)(17) also suggest the biosynthesis of BaP by anaerobic bacteria at the expense of lipids. A coworker of Mallet, Brisou (18) reports that it now seems possible to accept that:

(1) The biosynthesis of polybenzene hydrocarbons, including BaP for certain anaerobic bacteria occurs;

(2) This biosynthesis depends on only certain bacterial strains and is not a property vested in all the anaerobes; and

(3) This biosynthesis has for a starting point not only lipids (purified fatty acids), but other substrates (particularly aliphatic terpenes).

However, in a recent paper, Hase and Hites (19) found no biosynthesis of PAH by anaerobic bacteria present in New England river sediments, but they did find that the bacteria accumulated PAH from the sediments.

The PAH compounds also occur naturally as minerals (20). These relatively rare minerals, curtisite, idrialite and pendletonite, are found in association with mercury ores at scattered locations such as Shaggs Springs, Sonoma County, California and Ordejov, Czechoslovakia.

Geissman, Sim and Murdoch (1967) are cited by Blumer (20) as postulating that these minerals originated from organic matter by pyrolysis and were deposited by distillation or from solution. A pyrolytic origin is consistent with the fact that the minerals were found in association with bituminous substances and inflammable gases. The PAH and sulfur-containing composition of curtisite and idrialite is shown in Table 3.3. In contrast to the variety of PAH in these two minerals, pendletonite is almost pure coronene with only a small alkyl-derivative contribution.

Table 3.3: PAH and Sulfur-Containing Series in Curtisite and Idrialite

First Member Mass (amu)	Occurrence*	Suggested Structure	Chromatographic Position
216	CU	Benzofluorene (+ thienologs ?)	With chrysene
228	CU	Chrysene	(UV evidence)
234	(CU)	Tribenzothiophene	With chrysene
252	(CU)	4,5-10,11-dimethylenechrysene	With chrysene
254	CU	Naphthenochrysene (2 alicyclic carbons)	With alkylchrysenes
260	(CU)	Naphthenotribenzothiophene (2 alicyclic carbons)	With chrysene
266	CU, ID	Dibenzofluorene (+ thienologs ?)	With picene
276	(CU)	Anthanthrene	After picene (UV: not benzoperylene)
278	CU, ID	Picene	(UV evidence)
284	CU, ID	Tetrabenzothiophene	Before picene
296	CU	Dinaphthenobenzofluorene (3 alicyclic C/ring)	With benzofluorene
300	(CU)	Coronene	With anthanthrene

(continued)

Table 3.3: (continued)

First Member Mass (amu)	Occurrence*	Suggested Structure	Chromatographic Position
302	(CU)	Dibenzofluoranthene, dimethyl- enepicene	After picene
304	*ID*, CU	Naphthenopicene (2 alicyclic C)	With picene
310	(ID)	Naphthenotetrabenzothiophene (2 alicyclic C)	With tetrabenzothiophene
316	*ID*, (CU)	Tribenzofluorene	After picene
322	ID	Dinaphthenotetrabenzothio- phene (3 alicyclic C)	With picene/tetrabenzo- thiophene
328	ID	Benzopicene	After picene, with tribenzo- fluorene
334	ID	Pentabenzothiophene	With alkylpicenes
340	(ID)	Tetranaphthenopicene (5 alicyclic C)	With alkylpicenes
354	ID	Naphthenobenzopicene (2 alicyclic C)	With benzopicene
366	(ID)	Tetrabenzofluorene	Last PAH fraction
372	(ID)	Dinaphthenopentabenzothio- phene (3 alicyclic C)	After picene
378	(ID)	Dibenzopicene	Last PAH fraction

*CU is curtisite; ID is idrialite. Major series in italics; minor series in parentheses.

Source: Reference (20) as cited in ORNL/EIS-95

More recently, Blumer (21) proposed mechanisms for the geosynthesis of aro-
matic hydrocarbon minerals such as idrialite, curtisite and pendletonite. They
arise from sediments containing organic compounds that are located deeper in
the earth than those regions in which petroleum is formed and in which pyro-
lytic temperatures may reach 500°C. Although Blumer's mineral specimens came
from museum collections, it was believed that they were representative of the
original composition in situ since no contamination peaks were detected by mass
spectrometry (20).

Volcanic activity and forest fires are also sources of background PAH (13). For
est fires especially can be important in determining background levels, particu-
larly in the atmosphere. Also, Blumer and Youngblood (22) and Youngblood
and Blumer (23) suggest that PAH compounds in soils and recent sediments are
formed largely from natural forest and prairie fires. This suggestion is based on
the high degree of similarity in the molecular weight distribution of the many
series of alkyl homologs in the PAH compounds, and the fact that this distribu-
tion exhibits little variance over a wide range of depositional environments. Ta
ble 3.6 (in the next section) indicates that 140 tons of BP are emitted each yea
as a result of the open burning of forest and agricultural land as compared with
the 192 tons emitted per year by coke production.

Hydrocarbons, including PAH, are ubiquitous in the environment, and their pres
ence cannot be attributed exclusively to man's activities.

EXISTING CONCENTRATIONS

Existing concentrations of PAH include those from natural and anthropogenic sources. These sources release PAH compounds into the water environment (24) (Table 3.4) and atmosphere (25) (Table 3.5). Table 3.4 indicates the PAH compounds commonly found in water along with information about their relative carcinogenicity; Table 3.5 lists polycyclic compounds found in air, those that occur in cigarette smoke and exhaust gas and those that are associated with coal.

Table 3.4: PAH Commonly Found in Water

IUPAC Name*	Earlier Name**	Mol Wt	Relative Carcino-genicity***	Abbreviation
Anthracene	Anthracene	178	?	An
Benzo[a] anthracene	1,2-Benzanthracene	228	+	BaA
Benzo[b] fluoranthene	3,4-Benzfluoranthene	252	++	BbF
Benzo[j] fluoranthene	10,11-Benzfluoranthene	252	++	BjF
Benzo[k] fluoranthene	11,12-Benzfluoranthene	252	—	BkF
Benzo[a] pyrene	3,4-Benzpyrene	252	+++	BaP
Benzo[e] pyrene	1,2-Benzpyrene	252	+	BeP
Benzo[ghi] perylene	1,12-Benzperylene	276	—	BghiP
Chrysene	Chrysene	228	+	Ch
Fluoranthene	Fluoranthene	202	—	Fl
Indeno[1,2,3-cd] pyrene	2,3-o-Phenylenepyrene	276	+	IP
Phenanthrene	Phenanthrene	178	?	Ph
Perylene	Perylene	252	—	Per
Pyrene	Pyrene	202	—	Pyr

*IUPAC 1957 rules. 1960. *J. Am. Chem. Soc.* 82:5545-84.
**Pre-1957 naming.
***Relative activity on mouse epidermis: +++, active; ++, moderate; +, weak; ?, unknown; —, inactive.

Source: Reference (24) as cited in ORNL/EIS-95

Table 3.5: Polycyclic Compounds Found in Air, Cigarette Smoke, and Exhaust Gases

Compound*	Occurrence**
Naphthalene	A,T
2-Methylnaphthalene	A,T
Alkylnaphthalenes	A
Azulene	A,T
Acenaphthene	A,T
Acenaphthylene	A,T
Dibenzofuran	A
Carbazole	A
Dibenzothiophene	A
Fluorene	A,T
Anthracene (A)	A,T
Phenanthrene	A,T
2-Methylanthracene	T
11H-Benzo[b] fluorene	A

(continued)

Table 3.5: (continued)

Compound*	Occurrence**
	A,T
11H-Benzo[a] fluorene	A
7H-Benzo[c] fluorene	A,T
Fluoranthene (Fluor)	T
8-Methylfluoranthene	T
Alkyl fluoranthene	G
Naphthacene	A,T
Benz[a] anthracene (BaA)***,†	A,T
Chrysene (Ch)***,†	T
Alkyl chrysene	T
Benzo[c] phenanthrene***	A,T,G,D
Pyrene (P)	A,T
1-Methylpyrene	T
4-Methylpyrene	A
2,7-Dimethylpyrene	T
Naphtho[2,1,8,7-klmn] xanthene	T
10,11-Dihydro-9-H-benzo[a] cyclopent[i] anthracene	T
2,3-Dihydro-1-H-benzo[a] cyclopent[h] anthracene	T
7H-Dibenzo[c,g] carbazole***	A,T,G,D
Benzo[b] fluoranthene***	A,T
Benzo[ghi] fluoranthene	A,T
Benzo[j] fluoranthene***,†	A,T,G,D
Benzo[k] fluoranthene (BkF)	T
2-Methylfluoranthene***	T
Methylfluoranthene	T
Benzo[a] naphthacene	T,G,D
Dibenzo[b,h] phenanthrene	T
Dibenz[a,h] anthracene***,†	A,T,G,D
Benzo[a] pyrene (BaP)***,†	T
Methylbenzo[a] pyrene	T
Hydroxybenzo[a] pyrene	A
Benzo[a] pyrenequinone	A,T
Benzo[e] pyrene (BeP)***,†	A,T
Perylene (Per)	A,G,D
Dibenzo[a,l] naphthacene	T
Dibenzo[a,j] naphthacene	T
Naphtho[2,1,8-qra] naphthacene (Naphtho[2,3-a] pyrene)	A
Phenalen-1-one	A,T
Dibenzo[a,i] pyrene***,†	T,G,D
Dibenzo[a,e] pyrene	A,T,G,D
Dibenzo[cd,jk] pyrene (anthanthrene)	A
Dibenzo[cd,jk] pyrene-6,12-dione (anthanthrone)	A,T,G,D
Benzo[ghi] perylene (BghiP)	G
Dibenzo[b,pqr] perylene	A,T
Coronene (Cor)	A,T
Dibenzo[a,h] pyrene***,†	T
Tribenzo[a,i] fluorene	T
13H-Dibenzo[a,i] fluorene	T
Dibenzo[a,c] naphthacene	A
Benzo[h] quinoline	A
Ra-Benzo[h] quinoline††	A
Rb-Benzo[h] quinoline††	A,G
Benz[c] acridine†††	A
Ra-Benz[c] acridine††	

(continued)

Table 3.5: (continued)

Compound*	Occurrence**
Rb-Benz[c] acridine††	A
Dibenz[a,h] acridine***·†††	A,T
Indeno[1,2,3-ij] isoquinoline	A,G
Phenanthridine	A
11H-Indeno[1,2-b] quinoline	A
Acridine	A
Benzo[f] quinoline††	A
Ra-Benzo[f] quinoline††	A
Rb-Benzo[f] quinoline††	A
Benz[a] acridine††	A
Rb-Benz[a] acridine††	A
Dibenz[a,j] acridine***·†††	A,T
Rb-Dibenz[a,j] acridine	A
7H-Benz[de] anthracen-7-one	A
Indeno[1,2,3-cd] pyrene***·†	A
Dibenz[e,l] pyrene***	A
Xanthene-9-one	A
Dibenz[a,i] acridine	A

*Abbreviations used for most common compounds in parentheses
**A, air; T, tobacco smoke; G, gasoline exhaust; D, diesel exhaust
***Reported by Public Health Services to have carcinogenic activity
†Coal-associated PAH
††R, alkyl groups, substituted alkyl groups; Ra and Rb, various substitutes
†††Coal-associated heterocyclics

Source: Reference (25) as cited in ORNL/EIS-95

Air

The yearly global emission of BP, from data for 1966–1969, is estimated by Suess (13) to be about 5,000 tons, the greatest contribution coming from coal combustion (Table 3.6); U.S. yearly emission of BP was estimated to be about 25% of the worldwide total, or 1,283 tons. In comparison, Olsen and Haynes (26) estimate the U.S. annual BaP emissions to be 481 tons (Table 3.7) by assuming an annual consumption and emission rate that was derived from a large number of sources.

Measured average annual airborne BaP concentrations for 1966–1970 in urban areas in the United States are reported in Table 3.8. Altoona, Pennsylvania appears to have the highest recorded value (29.5 ng/m³ in 1967), followed by Chattanooga, Tennessee (22.9 ng/m³ in 1967). The U.S. average BaP concentration for the five-year period is about 2.0 ng/m³.

Table 3.9 lists nonurban annual average BaP concentrations for 1966–1970. As expected, these values are generally an order of magnitude less than those for the urban concentration in Table 3.8. Clarion County, Pennsylvania, which had the highest values for each of the 5 years (1.5, 2.1, 1.0, 1.2 and 1.2 ng/m³), compares favorably with most urban sites, but the values are only a fraction of the highest values recorded at some of the Pennsylvania urban sampling stations (e.g., Pittsburgh, 13.8 ng/m³ in 1969).

Table 3.6: Estimated BaP Emissions to the Atmosphere

Sources of Formation	BaP Emission (tons/yr) U.S.A.	Worldwide*	Worldwide
Heating and power generation, using			
Coal	431	1,945	2,376
Oil	2	3	5
Gas	2	1	3
Wood	40	180	220
Subtotal	475	2,129	2,604
Industrial processes			
Coke production	192	841	1,033
Catalytic cracking	6	6	12
Subtotal	198	847	1,045
Refuse and open burning			
Enclosed incineration			
Commercial and industrial	23	46	69
Other	11	22	33
Open burning			
Coal refuse fires	340	340	680
Forest and agriculture	140	280	420
Other	74	74	148
Subtotal	588	762	1,350
Vehicles			
Trucks and buses	12	17	29
Automobiles	10	6	16
Subtotal	22	23	45
Grand total	1,283	3,761	5,044

*Excluding U.S.A.

Source: Reference (13) as cited in ORNL/EIS-95

Table 3.7: Estimated Annual BaP Emissions for the United States

Source	Estimated BaP Emission Rate	Estimated Annual Consumption or Production	Estimated Annual BaP Emission
.....................Heat Generation.......................			
	(μg/10^6 Btu)	(10^{15} Btu)	(tons)
Coal			
Residential			
Hand-stoked	1,400,000	0.26	400
Underfeed	44,000	0.20	9.7
Commercial	5,000	0.51	2.8
Industrial	2,700	1.95	5.8
Electrical	90	6.19	0.6
Oil	200	6.79	1.5
Gas	100	10.57	1.2
Total			421.6

(continued)

Table 3.7: (continued)

Source	Estimated BaP Emission Rate	Estimated Annual Consumption or Production	Estimated Annual BaP Emission
. . . . Refuse Burning			
	(μg/ton)	(10^6 tons)	(tons)
Incineration			
Municipal	5,300	18	0.1
Commercial	310,000	14	4.8
Open burning			
Municipal refuse	310,000	14	4.8
Grass, leaves	310,000	14	4.8
Auto components	26,000,000	0.20	5.7
Total			20.2
. . . . Industry			
	(μg/bbl)	(10^6 bbl)	(tons)
Petroleum catalytic cracking*			
Fluid catalytic cracker			
No CO boiler**	240	790	0.21
With CO boiler	14	790	0.012
Houdriflow catalytic cracker			
No CO boiler	218,000	23.3	5.6
With CO boiler	45	43.3	0.0024
Thermo for catalytic cracker***			
No CO boiler	90,000	131	13.0
With CO boiler	<45	59	<0.0029
Thermo for catalytic cracker†			
No CO boiler	—	119	0.0041
With CO boiler	<31	0	0
Asphalt road mix	50 μg/ton	187,000 tons	0.000010
Asphalt air blowing	<10,000 μg/ton	4,400 tons	<0.000048
Carbon-black manufacturing	††	††	††
Steel and coke manufacturing	††	††	††
Chemical complex	††	††	††
Total			18.8
. . . . Motor Vehicles			
	(μg/gal)	(10^{10} gal)	(tons)
Gasoline			
Automobiles	170	4.61	8.6
Trucks	>460	2.01	>10
Diesel	690	0.257	2.0
Total			>20.6
Total (all sources tested)			481

*Catalyst regeneration.

**CO boiler—carbon monoxide waste heat boiler.

***Air lift.

†Bucket lift.

††Atmospheric samples indicate that BaP emissions from these processes are not extremely high.

Table 3.8: Annual Average Ambient BaP Concentrations at
National Air Sampling Network Urban Stations (ng/m³)

Station	1966	1967	1968	1969	1970
Alabama					
Birmingham	18.5	—	—	—	—
Gadsden	3.5	—	2.4	1.8	2.5
Huntsville	—	3.1	2.7	1.8	1.6
Mobile	6.5	—	4.2	2.6	—
Montgomery	—	2.3	2.9	2.0	1.3
Alaska					
Anchorage	2.3	1.9	1.7	1.3	0.8
Arizona					
Phoenix	1.7	2.5	2.1	2.2	—
Tucson	0.6	0.7	0.7	0.5	0.4
Arkansas					
Little Rock	1.2	0.9	0.9	1.1	0.7
West Memphis	1.1	2.2	2.2	2.4	0.6
California					
Burbank	2.5	—	—	2.9	1.9
Glendale	—	1.0	1.6	1.6	1.0
Long Beach	—	2.1	2.1	2.3	1.0
Los Angeles	2.1	1.3	1.8	1.9	1.2
Oakland	2.7	1.7	1.6	1.6	1.0
Ontario	—	—	0.9	0.6	0.6
Pasadena	1.8	—	2.3	—	0.7
Riverside	—	—	1.3	0.8	0.7
Sacramento	—	—	1.4	1.8	0.7
San Bernardino	—	—	1.0	0.9	0.8
San Diego	1.7	1.6	1.2	1.4	0.7
San Francisco	1.1	1.5	1.8	1.2	0.6
Colorado					
Denver	2.3	2.4	2.3	2.5	2.2
Connecticut					
Hartford	2.3	2.1	1.4	2.0	1.4
New Haven	3.5	1.9	1.4	2.1	1.2
Delaware					
Newark	1.0	1.4	0.9	—	0.4
Wilmington	2.2	2.7	1.9	1.7	1.1
District of					
Columbia	2.4	1.9	1.9	4.3	—
Florida					
Jacksonville	—	—	2.9	2.3	1.4
Tampa	—	—	1.5	1.0	0.5
Georgia					
Atlanta	1.4	3.0	1.8	1.9	0.9
Hawaii					
Honolulu	0.2	0.5	0.6	0.6	0.2
Idaho					
Boise City	3.5	2.4	2.0	6.0	1.1
Illinois					
Chicago	3.3	3.0	3.1	3.9	2.0
Springfield	—	—	1.1	1.3	0.9
Indiana					
East Chicago	6.8	5.7	1.9	6.8	5.3
Hammond	3.9	2.5	2.1	3.3	1.7
Indianapolis	10.4	5.7	4.1	5.2	2.3
Muncie	2.4	1.6	—	—	—
New Albany	5.4	—	—	4.3	3.7
South Bend	2.2	2.6	3.7	3.7	2.4
Terre Haute	—	3.7	—	4.0	2.8
Iowa					
Davenport	3.2	—	—	1.7	0.9
Des Moines	2.5	2.7	1.1	0.9	0.7
Cedar Rapids	—	0.8	0.7	—	0.3
Kansas					
Kansas City	1.2	—	1.2	1.1	2.4
Topeka	—	0.5	0.7	0.4	0.3
Wichita	0.8	0.5	1.0	0.7	0.5

(continued)

Table 3.8: (continued)

Station	1966	1967	1968	1969	1970
Kentucky					
Ashland	10.5	—	9.3	10.9	6.7
Covington	3.1	1.9	3.6	4.1	4.4
Lexington	—	1.8	3.0	—	1.6
Louisville	2.5	2.1	2.7	1.9	—
Louisiana					
New Orleans	2.3	1.8	1.6	1.5	1.1
Maine					
Portland	—	—	2.3	—	1.1
Maryland					
Baltimore	2.8	3.8	2.3	2.8	2.1
Massachusetts					
Worcester	—	—	1.7	1.5	1.6
Michigan					
Detroit	4.7	5.4	5.1	3.9	2.6
Flint	—	1.4	0.8	1.7	1.5
Grand Rapids	—	2.8	3.4	1.7	0.9
Trenton	—	—	1.4	1.6	0.8
Minnesota					
Duluth	2.2	—	2.7	2.1	1.1
Minneapolis	1.6	1.3	1.1	1.4	0.6
Moorhead	0.7	—	0.9	1.0	1.6
St. Paul	1.8	2.3	1.8	1.8	1.0
Missouri					
Kansas City	—	—	1.8	1.6	1.1
St. Louis	—	2.3	—	3.3	—
Montana					
Helena	—	0.8	0.9	0.5	—
Nebraska					
Omaha	2.7	1.3	1.9	1.6	1.0
Nevada					
Las Vegas	1.3	1.1	1.4	—	—
Reno	—	4.6	3.1	—	—
New Hampshire					
Concord	0.6	1.5	1.0	0.7	0.6
New Jersey					
Camden	3.0	—	1.6	2.4	1.9
Glassboro	0.7	0.8	1.2	1.1	1.2
Jersey City	4.2	3.5	2.3	2.7	4.7
Marlton	1.2	1.6	1.3	—	1.4
Newark	2.1	3.3	2.1	1.8	1.5
Paterson	—	1.9	2.0	1.2	1.2
Perth Amboy	2.1	2.1	1.2	1.2	1.0
Trenton	2.2	—	1.0	1.5	1.1
New Mexico					
Albuquerque	2.0	1.9	1.8	1.1	1.1
New York					
New York City	4.1	3.9	—	3.6	3.0
North Carolina					
Charlotte	5.7	6.3	5.6	4.9	1.9
Durham	—	—	8.0	3.4	3.9
North Dakota					
Bismarck	—	—	0.9	1.0	0.4
Ohio					
Akron	4.1	3.7	3.0	—	—
Cincinnati	3.6	1.9	1.8	2.9	2.6
Cleveland	3.1	2.9	3.0	3.8	2.8
Columbus	2.9	1.7	2.2	2.7	1.6
Dayton	2.7	3.7	2.4	1.9	1.5
Toledo	1.8	1.9	1.8	1.5	1.4
Youngstown	7.3	8.2	5.6	9.9	7.1
Oklahoma					
Oklahoma City	1.5	0.7	0.7	0.7	0.9
Tulsa	0.7	0.6	0.8	0.5	0.8

rbons

tions at
g/m')

1970

2.5
1.8
--
1.3

0.8

--
0.4

0.7
0.8

1.9
1.0
1.0
1.2
1.0
0.8
0.7
0.7
0.7
0.8
0.7
0.6

2.2

1.4
1.2

0.4
1.1

--

1.4
0.5

0.9

0.2

1.1

2.0
0.9

5.3
1.7
2.3
--
3.7
2.4
2.8

0.9
0.7
0.3

2.4
0.3
0.5
(continued)

Table 3.8: (continued)

Station	1966	1967	1968	1969	1970
Kentucky					
Ashland	10.5	—	9.3	10.9	6.7
Covington	3.1	1.9	3.6	4.1	4.4
Lexington	—	1.8	3.0	—	1.6
Louisville	2.5	2.1	2.7	1.9	—
Louisiana					
New Orleans	2.3	1.8	1.6	1.5	1.1
Maine					
Portland	—	—	2.3	—	1.1
Maryland					
Baltimore	2.8	3.8	2.3	2.8	2.1
Massachusetts					
Worcester	—	—	1.7	1.5	1.6
Michigan					
Detroit	4.7	5.4	5.1	3.9	2.6
Flint	—	1.4	0.8	1.7	1.5
Grand Rapids	—	2.8	3.4	1.7	0.9
Trenton	—	—	1.4	1.6	0.8
Minnesota					
Duluth	2.2	—	2.7	2.1	1.1
Minneapolis	1.6	1.3	1.1	1.4	0.6
Moorhead	0.7	—	0.9	1.0	1.6
St. Paul	1.8	2.3	1.8	1.8	1.0
Missouri					
Kansas City	—	—	1.8	1.6	1.1
St. Louis	—	2.3	—	3.3	—
Montana					
Helena	—	0.8	0.9	0.5	—
Nebraska					
Omaha	2.7	1.3	1.9	1.6	1.0
Nevada					
Las Vegas	1.3	1.1	1.4	—	—
Reno	—	4.6	3.1	—	—
New Hampshire					
Concord	0.6	1.5	1.0	0.7	0.6
New Jersey					
Camden	3.0	—	1.6	2.4	1.9
Glassboro	0.7	0.8	1.2	1.1	1.2
Jersey City	4.2	3.5	2.3	2.7	4.7
Marlton	1.2	1.6	1.3	—	1.4
Newark	2.1	3.3	2.1	1.8	1.5
Paterson	—	1.9	2.0	1.2	1.2
Perth Amboy	2.1	2.1	1.2	1.2	1.0
Trenton	2.2	—	1.0	1.5	1.1
New Mexico					
Albuquerque	2.0	1.9	1.8	1.1	1.1
New York					
New York City	4.1	3.9	—	3.6	3.0
North Carolina					
Charlotte	5.7	6.3	5.6	4.9	1.9
Durham	—	—	8.0	3.4	3.9
North Dakota					
Bismarck	—	—	0.9	1.0	0.4
Ohio					
Akron	4.1	3.7	3.0	—	—
Cincinnati	3.6	1.9	1.8	2.9	2.6
Cleveland	3.1	2.9	3.0	3.8	2.8
Columbus	2.9	1.7	2.2	2.7	1.6
Dayton	2.7	3.7	2.4	1.9	1.5
Toledo	1.8	1.9	1.8	1.5	1.4
Youngstown	7.3	8.2	5.6	9.9	7.1
Oklahoma					
Oklahoma City	1.5	0.7	0.7	0.7	0.9
Tulsa	0.7	0.6	0.8	0.5	0.8

(continued)

Table 3.8: (continued)

Station	1966	1967	1968	1969	1970
Oregon					
Eugene	—	2.4	—	—	—
Medford	—	4.8	8.2	4.1	—
Portland	3.3	3.5	4.1	2.6	2.3
Pennsylvania					
Allentown	—	1.8	1.2	1.9	2.4
Altoona	—	29.5	18.0	22.3	19.3
Bethlehem	—	2.9	2.1	2.0	2.7
Harrisburg	—	—	1.3	1.5	1.5
Lancaster	2.3	—	—	—	—
Philadelphia	3.8	5.9	2.9	4.0	2.4
Pittsburgh	4.9	7.0	6.3	13.8	5.9
Reading	2.3	2.9	2.4	1.8	1.6
Scranton	—	5.2	6.1	7.7	2.9
Warminster	0.9	2.2	0.9	1.0	—
West Chester	—	1.1	1.0	1.3	—
Wilkes Barre	—	—	1.6	1.5	1.3
York	—	1.8	1.9	2.0	1.2
Rhode Island					
East Providence	—	1.6	1.2	1.2	1.2
Providence	3.6	2.8	2.0	2.2	2.1
South Carolina					
Columbia	—	4.2	6.2	1.3	—
Greenville	5.0	—	18.6	7.0	3.4
Tennessee					
Chattanooga	8.4	22.9	7.4	4.2	5.5
Knoxville	—	7.0	9.8	4.7	—
Memphis	1.7	1.6	1.3	0.7	1.4
Nashville	5.5	7.0	6.0	2.8	2.6
Texas					
Dallas	1.4	—	—	2.0	1.9
Houston	0.9	—	—	—	1.2
San Antonio	0.6	1.4	0.9	0.6	1.0
Utah					
Ogden	0.5	—	0.8	0.7	2.5
Salt Lake City	1.2	0.7	1.0	0.7	1.4
Vermont					
Burlington	0.8	—	0.7	0.5	0.7
Virginia					
Danville	3.2	—	2.5	1.8	2.7
Hampton	—	2.2	1.5	0.9	1.1
Lynchburg	—	9.2	8.7	6.3	4.5
Norfolk	2.8	3.5	4.9	3.9	1.8
Portsmouth	—	7.7	10.2	3.4	4.9
Richmond	—	5.2	—	2.2	2.1
Roanoke	—	7.5	7.7	5.3	6.2
Washington					
Seattle	2.7	1.8	2.0	1.6	1.5
West Virginia					
Charleston	3.4	—	4.6	2.6	2.1
Wisconsin					
Kenosha	—	—	1.4	1.7	1.3
Madison	—	—	1.3	—	1.1
Milwaukee	4.1	—	4.7	4.0	2.5
Superior	—	—	3.3	1.6	1.5
Wyoming					
Casper	—	—	0.9	0.6	0.4
Cheyenne	0.5	—	0.6	0.5	0.4

Source: Reference (25) as cited in ORNL/EIS-95

1969	1970
--	--
4.1	
2.6	2.3
1.9	2.4
22.3	19.3
2.0	2.7
1.5	1.5
-	--
4.0	2.4
13.8	5.9
1.8	1.6
7.7	2.9
1.0	-
1.3	-
1.5	1.3
2.0	1.2
1.2	1.2
2.2	2.1
1.3	-
7.0	3.4
4.2	5.5
4.7	-
0.7	1.4
2.8	2.6
2.0	1.9
-	1.2
0.6	1.0
0.7	2.5
0.7	1.4
0.5	0.7
1.8	2.7
0.9	1.1
6.3	4.5
3.9	1.8
3.4	4.9
2.2	2.1
5.3	6.2
1.6	1.5
2.6	2.1
1.7	1.3
-	1.1
4.0	2.5
1.6	1.5
0.6	0.4
0.5	0.4

Table 3.9: Annual Average Ambient BaP Concentrations at National Air Sampling Network Nonurban Stations (ng/m³)

Station	1966	1967	1968	1969	1970
Arizona					
Grand Canyon	0.3	0.2	0.2	0.2	0.1
Maricopa County	-	0.2	0.5	0.3	0.3
Arkansas					
Montgomery County	0.3	0.1	0.2	0.2	0.1
California					
Humboldt County	0.4	0.4	0.3	0.5	0.1
Idaho					
Butte County	-	-	0.2	0.1	0.1
Indiana					
Monroe County	0.5	-	0.5	0.3	0.2
Parke County	0.9	-	0.4	0.3	0.4
Maine					
Acadia National Park	0.2	-	0.3	0.1	0.2
Missouri					
Shannon County	-	0.2	0.2	0.2	0.2
Montana					
Glacier National Park	-	0.3	0.4	0.4	-
Nebraska					
Thomas County	0.2	-	0.2	0.1	0.1
Nevada					
White Pine County	0.1	-	0.1	0.1	0.1
New Hampshire					
Coos County	0.2	0.2	0.2	0.1	0.1
New York					
Jefferson County	0.2	-	0.2	0.3	0.2
North Carolina					
Cape Hatteras	0.2	-	0.2	0.1	0.2
Oklahoma					
Cherokee County	0.2	0.2	0.2	0.2	0.2
Oregon					
Curry County	0.1	1.1	0.1	0.1	0.1
Pennsylvania					
Clarion County	1.5	2.1	1.0	1.2	1.2
Texas					
Matagorda County	0.3	0.1	0.2	0.1	0.3
Vermont					
Orange County	0.9	-	0.3	0.3	0.2
Virginia					
Shenandoah National Park	0.9	0.3	0.3	0.3	0.2

Source: Reference (25) as cited in ORNL/EIS-95

Table 3.10 demonstrates the seasonal effect on BaP concentrations in urban air; concentrations are higher in winter than in summer, the difference often being an order of magnitude.

Shabad (27) cites Yanysheva and Balenko (1966) in reporting the safe lifetime BP dose for the human lungs as 4.3 mg. On the basis of this value, the concentration of atmospheric BP should not exceed 120 ng/m³. A recent standard of BaP concentration (28) for industrial workers was determined to be 200 ng/m³,

about twice as great as the suggested atmospheric value. The highest recorded BaP value in the United States for 1966-1970 (29.5 ng/m³ in 1967 for Altoona, Pennsylvania, Table 3.8) is almost an order of magnitude less than the proposed industrial standard and fourfold less than the atmospheric standard.

Table 3.10: Seasonal Effect on the BaP Concentrations
of Various Urban Atmospheres

| Location | Year | .... Concentrations .... (µg/m³ of air) .... | |
		Summer (low)	Winter (high)
Atlanta, GA	1958	0.0016	0.015
	1960	0.0009	0.014
Birmingham, AL	1958	0.006	0.074
	1960	0.003	0.062
Cincinnati, OH	1958	0.002	0.026
	1960	0.0012	0.018
Detroit, MI	1958	0.0034	0.031
Location I	1961	0.0072	0.017
Location II	1961	0.0036	0.0137
Location III	1963	0.0002	0.0018
Los Angeles, CA	1958	0.0004	0.013
Nashville, TN	1958	0.0014	0.055
New Orleans, LA	1958	0.0020	0.006
	1960	0.0006	0.007
New York, NY			
Herald Square	1963-64	0.0005	0.0094
Columbus Circle	1964	0.0007	0.0026
Philadelphia, PA	1958	0.0025	0.019
San Francisco, CA	1958	0.0003	0.0075
South Charleston, WV	1960	0.0006	0.012

Source: Reference (26) as cited in ORNL/EIS-95

Water

According to the NAS report (29), about 6 million tons of petroleum hydrocarbons enter the oceans annually; the major contributors are marine transportation and runoff (urban and river), yielding 2.1 and 1.9 million tons per year respectively (Table 3.11). Coastal refineries and industrial and domestic waste together were estimated to contribute 0.8 million tons per year; natural seeps and atmospheric fallout each add another 0.6 million tons per year.

Table 3.12 shows the concentration of BP in marine sediments, primarily off the Mediterranean coast. These sediments are muds, sands, and shells; there is no easily discernible correlation between sediment, depth of sample, or BP concentration.

Concentrations of PAH in surface waters, mainly German rivers, are compiled in Table 3.13 (multiple values correspond to different sources of the same information). The average total PAH concentration is about 1.2 µg/ℓ; the highest values (12 µg/ℓ) are recorded in samples taken at the discharge site of shale oil and coke by-product effluent. However, 500 to 3,500 m downstream of the effluent discharge, concentrations are reduced to 1-2 µg/ℓ. The PAH levels in Thames

River water are comparable with those in the German rivers (24).

Table 3.11: Comparison of Estimates for Petroleum Hydrocarbons Annually Entering the Ocean, 1969-1971

	Authority (millions of tons per year)		
	MIT SCEP	USCG Impact	NAS
	Report*	Statement**	Workshop
Source	(1970)	(1973)	(1973)
Marine transportation	1.13	1.72	2.133
Offshore oil production	0.20	0.12	0.08
Coastal oil refineries	0.30		0.2
Industrial waste		1.98	0.3
Municipal waste	0.45		0.3
Urban runoff			0.3
River runoff***			1.6
Subtotal	2.08	3.82	4.913
Natural seeps			0.6
Atmospheric rainout	9.0†		0.6
Total	11.08		6.113

*From Study of Critical Environmental Probe (SCEP). 1970. *Man's impact on the global environment. Assessment and recommendations for action*. Cambridge, MA. MIT Press.

**From U.S. Coast Guard. 1973. *Draft environmental impact statement*. For International Convention for the Prevention of Pollution from Ships, 1973.

***Input from recreational boating assumed to be incorporated in the river runoff value.
†Based upon assumed 10% return from the atmosphere.

Source: Reference (29) as cited in ORNL/EIS-95

Table 3.12: Concentration of BP in Marine Sediments

Source	Sample	Depth (m)	BP Concentration (µg/kg of dry sample)
Greenland, West Coast	Sand	0.20	5
Italy, Bay of Naples	Mud, sand, shell*	15-45	1,000-3,000
(6 locations)	Sand, shell	13	7.5
	Mud, sand	2-65	10-530
	Mud, sand, shell**	55	260-960
	Muddy sand	120	1.4
	Mud, sand***		100-560
French Mediterranean Coast		0-0.03	1,800
		0.03-0.08	3,600
		0.08-0.13	5,000
		0.13-0.18	2,500
		0.23-0.28	2,200
		0.33-0.38	730
		0.48-0.53	420
		1.00	26
		2.00	16
	Sand	14	400
	Black mud	16	1,500
	Sand	48	75
	Sand	53	Traces
	Beige mud	82	400

(continued)

Table 3.12: (continued)

Source	Sample	Depth (m)	BP Concentration (μg/kg of dry sample)
Estuary, French Mediterranean	Sand		34
	Sand	1	20
	Sand	4	15
	Sand	5	25
	Mud	102	Not detected
French Mediterranean Coast			50
French Mediterranean Coast			20
French Channel Coast	Mud		15,000
French Channel and Atlantic Coasts (11 locations)	Mud, sand		Not detected to 1,700

*Five samples were collected 300 m from shore, area is highly industrialized.
**Four samples were collected in the vicinity of volcanic pollution.
***Four samples; this island is affected by pollution.

Source: Reference (4) as cited in ORNL/EIS-95

Table 3.13:   Concentration of PAH in Surface Waters

	.... Concentration (μg/ℓ)		
Source	BP	Carcinogenic PAH	Total PAH
Bodensee		0.003	
		0.0004*	
	0.0013	0.030	0.065
Alprhine		0.005*	
River Rhine		0.050-0.500**	
River Rhine at Mainz		0.080*	
River Rhine at Mainz			
(March 1964)	0.049	0.240	0.73
(March 1964)	0.114	0.730	1.50
River Main, at Seligenstadt	0.0024	0.155	0.48
River Danube, at Ulm			
(April 1964)	0.0006	0.055	0.28
(May 1964)		0.078	0.20
River Gersprenz, at Munster			
(January 1964)	0.0096	0.055	0.16
(April 1964)		0.038	0.12
River Aach, at Stockach*		0.050	
River Aach, at Stockach*			
Sample I	0.043	1.30	3.0
Sample II	0.016	0.90	2.5
Sample III	0.004	0.50	1.4
Sample IV	0.005	1.10	3.1
River Schussen (Bodensee)		0.50*	
River Schussen	0.01	0.20	1.0
River Argen (Bodensee)		0.07*	
River Seine	***		
River Plyussa			
At discharge site of shale-oil effluent	12		

(continued)

BP Concentration (µg/kg of dry sample)
34
20
15
25
Not detected
50
20
15,000
Not detected to 1,700

industrialized.
on.

Table 3.13: (continued)

Source	........Concentration (µg/ℓ)........		
	BP	Carcinogenic PAH	Total PAH
3,500 m downstream	1		
At the water intake of Narva A river	0.1		
15 m below discharge of coke by-product effluent	8-12		
500 m downstream	2-3		
Peat (turf) water	0.05		

*Extrapolated from centrifugate fractions.
**Extrapolated from activated-carbon adsorption analyses.
***Considerable amount.

Source: Reference (4) as cited in ORNL/EIS-95

ɘ Waters

ו (µg/ℓ)	
ɘnic	Total PAH
।4*	
	0.065
ɔ0**	
,*	
	0.73
	1.50
	0.48
	0.28
	0.20
	0.16
	0.12
	3.0
	2.5
	1.4
	3.1
	1.0

(continued)

Concentrations of PAH have been detected in wastewater samples (Table 3.14). In many instances, domestic effluents have higher PAH concentrations than do factory effluents. The PAH levels in domestic sewage increase by 50- to 1,000-fold during periods of heavy rain (Table 3.15) due to increased runoff, primarily from highways (9). Table 3.16 shows the PAH content of road dust and a comparison of it with the atmospheric dust of urban air in Dortmund, a large German city. Many of the PAH concentrations in road dust are more than 1,000-fold those levels found in soil (Table 3.17). Also, the PAH concentrations in road dust are shown to be several times greater than those in the atmospheric dust of Dortmund. Therefore, it is evident why runoff from highways causes a dramatic increase in the PAH concentration found in sewage during a heavy rain as opposed to PAH sewage levels during dry weather (Table 3.15).

Table 3.14: PAH in Various Wastewater Samples (ng/ℓ)

PAH	........Effluents........			...Sewage*...	
	Domestic	Factory	Domestic		
Fluoranthene	2,416	2,198	273	3,420	2,660
Pyrene	1,763	1,957	—	3,120	2,560
Benzo[a]anthracene	319	167	191	1,360	343
Benzo[b]fluoranthene	202	114	36	870	525
Benzo[j]fluoranthene	205	45	37	1,740	1,100
Benzo[k]fluoranthene	193	32	31	460	336
Benzo[a]pyrene	74	100	38	100	368
Benzo[ghi]perylene	219	73	40	480	120
Indeno[1,2,3-cd]pyrene	238	57	22	930	476

*High percentage industry.

Source: References (9)(24) as cited in ORNL/EIS-95

Table 3.15: PAH in Domestic Sewage During Dry and Wet Weather (ng/ℓ)

PAH	Dry Weather	Heavy Rain
	. Concentration in Sewage During .	
Fluoranthene	352	16,350
Pyrene	254	16,050
Benzo [a] anthracene	25	10,360
Benzo [b] fluoranthene	39	9,910
Benzo [j] fluoranthene	57	10,790
Benzo [k] fluoranthene	22	4,180
Benzo [a] pyrene	1	1,840
Benzo [ghi] perylene	4	3,840
Indeno [1,2,3-cd] pyrene	17	4,980

Source: Reference (9)(24) as cited in ORNL/EIS-95

Table 3.16: PAH in Road Dust (mg/kg)

Substances Detected	Dust from Federal Road 31 1	2	3	4	5	Atmospheric Dust Dortmund
Fluoranthene	126	166	78	37	32	3.8
Pyrene	114	147	62	—	27	2.77
Benzo [a] anthracene	21.	59	19	17	16	0.53
Benzo [j] fluoranthene	60	97	36	14	6	0.62
Benzo [b] fluoranthene	26	62	19	18	15	0.16
Chrysene	22	64	—	—	—	—
Benzo [a] pyrene	9	17	12	2	3	0.05
Benzo [ghi] perylene	22	47	21	6	12	0.51
Benzo [k] fluoranthene	13	26	13	6	8·	0.48
Indeno [1,2,3-cd] pyrene	24.	61	20	8	9	0.96
Known compounds	437	746	280	108	128	9.88
Unidentified compounds	400	800	22	17	18	0.20
PAH total	837	1,546	302	125	146	10.08
Carcinogenic PAH	162	360	106	59	49	2.31
% fraction of carcinogens of the total amount	19	23	35	47	33	23
Number of substances isolated	32	32	22	20	20	18

Source: Reference (9)(24) as cited in ORNL/EIS-95

Table 3.17: Concentration of PAH Found in Forest Soil (µg/kg)

PAH	. .South of Darmstadt. . . Mixed Woods	Beech Woods	Oak Woods	. . Near Lake Constance. . Spruce Woods	Mixed Woods	Beech Woods
Benzo [a] pyrene	2.5	4.0	1.5	1.5	2.5	1.5
Benzo [ghi] perylene	10	70	20	10	20	10
Benzo [b] fluoranthene and benzo [j] fluoranthene	30	110	50	35	25	25

Source: Reference (9) as cited in ORNL/EIS-95

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et Weather (ng/l)

sge During .
Heavy Rain

16,350
16,050
10,360
9,910
10,790
4,180
1,840
3,840
4,980

3)

		Atmospheric
Road 31		Dust
4	5	Dortmund
37	32	3.8
–	27	2.77
17	16	0.53
14	6	0.62
18	15	0.16
–	–	–
2	3	0.05
6	12	0.51
6	8	0.48
8	9	0.96
108	128	9.88
17	18	0.20
125	146	10.08
59	49	2.31
47	33	23
20	20	18

rest Soil (μg/kg)

Near Lake Constance. .		
ruce	Mixed	Beech
ods	Woods	Woods
1.5	2.5	1.5
0	20	10
5	25	25

Soil

Concentrations of PAH in forest soil are listed in Table 3.17. The soil samples were taken from beech, oak, and mixed woods; in one location, soils from beech woods had the highest PAH concentrations, but in the other, soils from mixed woods had the highest levels. Thus, no apparent correlation between PAH concentration in soil and ground cover can be detected from this table.

FATE IN NATURAL WATER

The processes which affect PAH in the aquatic environment may be considered as two general types: those which result in transport, and those which result in transformation. Transport processes are those in which only the physicochemical form is altered, while transformational processes result in alteration to a different chemical species. As such, transport processes are driven by chemical equilibrium considerations, while transformational processes are essentially nonequilibrium. A second general distinction among transport and transformation processes is whether or not they are mediated by living organisms (biotic vs abiotic). Major transport processes in the aquatic environment are summarized in Table 3.18.

Table 3.18: Major Processes Influencing PAH Behavior in Natural Waters

	Transport	Transformation
Abiotic	Dispersion	Oxidation
	Sorption	Photolysis
	Volatilization	
Biotic	Bioaccumulation	Metabolism
		Microbial degradation

Source: NTIS CONF-790486-3

In natural stream systems, PAH will be transported to the ocean, decomposed, or removed. Removal can consist of consumption by biota, adsorption on biological material, and/or adsorption on suspended or bottom mineral matter (2). Decomposition depends on biological metabolism or chemical oxidation, whereas physical transport usually occurs in the absence of the other mechanisms. Transient storage compartments for hydrocarbons include water and organisms, whereas sediments probably constitute the most significant long-term storage site (Figure 3.1). Losses from an aqueous system include evaporation, tidal and riverine flushing, and microbiological decomposition (30).

Marine

In marine environments, pollutants are transported and distributed by currents, waves, and turbulent mixing. However, present information is insufficient to . predict accurately either the complete physical behavior or the entire biological fate of a pollutant in oceanic deep waters (31). For example, the fate of a pollutant may be determined as often by the microbial environments as by the chemical and physical surroundings. Many pollutants, including the components of crude oil, may be degraded by the action of bacterial yeasts and other microflora in either water or bottom sediments. In the event that a benthic population is altered or destroyed, the loss of microbial degradation may cause harmful chemicals to be released (these same chemicals ordinarily could be degraded by . a healthy benthic population).

Figure 3.1: Conceptual Model of Probable Flows of Hydrocarbons Through Major Compartments of an Estuarine Ecosystem
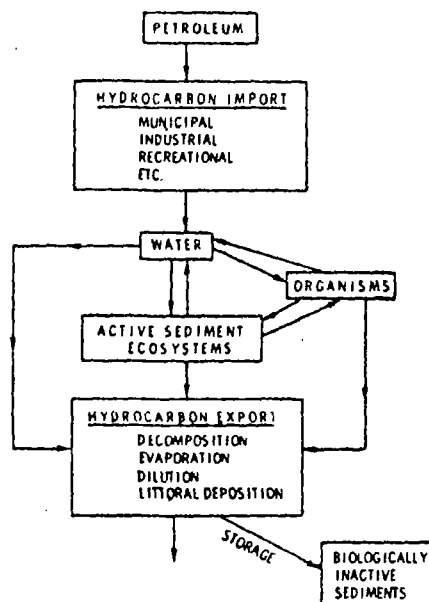
Source: Reference (30) as cited in ORNL/EIS-95

Most chemical reactions occur in the ocean at the air-sea interface, the sediment-water interface, or the boundaries between the water and the particles that are suspended in the water (32). Materials that concentrate at the air-water interface are subject to oxidation, ultraviolet radiation, evaporation of volatile constituents, and polymerization (32).

When considering the rate of sediment supply to the oceans and the apparent rate of accumulation in deep ocean basins, it is likely that 90% or more of river-borne particles are deposited on continental shelves. The particles that are greater than 0.5 μ in diameter have residence times in the oceanic water column of less than 100 years. For smaller particles the residence may be between 200 and 600 years. There is also rapid removal of particles by filter feeders that concentrate the particles in fecal pellets, which drop to the ocean bottom (32).

Accumulation in Biota

Upon entering the aquatic environment, hydrocarbons are available for uptake by the biota. Farrington and Quinn (33), in studying marine mollusks, report that marine organisms can synthesize some low-boiling hydrocarbons, but state that synthesis of naphthenic and aromatic hydrocarbons is too complex for those marine organisms. Thus, when hydrocarbons were extracted from clams collected in Narragansett Bay, they were identified as petroleum hydrocarbons because they included aromatic species. Marine mussels have also been recognized as good indicators of petroleum hydrocarbons. They appear to take up and re-

lease the hydrocarbons in proportion to the hydrocarbon concentrations in sur-rounding seawater (30). Lee, Sauerheber, and Benson (34) also report the presence of hydrocarbons in mussels. The experiments were performed in the laboratory on the marine mussel *Mytilus edulis*. The mussel rapidly filtered hydrocarbons across its gills, but seemed to lack the ability to metabolize any of the hydrocarbons. The nontoxic paraffinic hydrocarbons were taken up to a greater extent (10 mg per mussel) than were the aromatics (2 to 20 μg per mussel). When the polluted mussels were placed in uncontaminated seawater, they discharged the hydrocarbons: 90% of the heptadecane, 80% of the Tetralin (1,2,3,4-tetrahydronaphthalene), and most of the BaP; naphthalene and toluene were also discharged.

Other experiments by Lee and coworkers (35)(36) indicate that unlike mussels, marine copepods and the blue crab, *Callinectes sapidus*, have the ability to metabolize paraffinic and aromatic hydrocarbons. When transferred to fresh seawater, both copepod and blue crab released most of the accumulated radiolabeled hydrocarbons. After 17 days, the temperate water copepod *Calanus plumchrus* discharged all but 1×10^{-5} μg of benzypyrene of the original ingested amount, 22×10^{-4} μg. The hepatopancreas, assumed to be the main site of hydrocarbon metabolism, was the only organ in the blue crab where an appreciable buildup of radioactivity occurred. Based on later work, Lee and coworkers report that similar rates of hydrocarbon uptake, metabolism, and discharge have been observed in the California spiny lobster *Panulirus interruptus*, the spider crab *Libinia emarginata*, and the American lobster *Homarus Americanus*, leading to speculation that all marine crustaceans have the ability to metabolize hydrocarbons.

The oyster, a marine counterpart of the mussel, also has the ability to take up hydrocarbons. In one study (37), oysters from Galveston Bay were found to contain hydrocarbons, 56% of which were aromatic. Ehrhardt (37) considers the stability of hydrocarbons, as they pass through the food chain, responsible for uptake of the chemical by the oyster. In a study by Blumer (21), hydrocarbons in the liver of the basking shark were found to reflect the hydrocarbon content of its planktonic food. On the basis of this supporting evidence, Ehrhardt concludes that even highly organized animals accumulate the entire range of hydrocarbons to which they are exposed.

From laboratory studies of North Sea plankton, Whittle (38) proposed that plankton concentrate hydrocarbons from seawater, possibly via surface absorption; this further supports the accumulation of hydrocarbons by lower members of the aquatic food chain. Another indication that highly organized animals can take up hydrocarbons is from research by Ogata and Miyake (39). They demonstrated that aromatic hydrocarbons (benzene, xylene, and toluene) rapidly infiltrate fish and possibly impart an offensive odor. They conclude that aromatic hydrocarbons can accumulate in fish and that the hydrocarbons might be transferred to man through his consumption of fish.

Stegeman and Teal (40) also found hydrocarbon uptake in their laboratory study of the oyster, *Crassostrea virginica*. They note that the hydrocarbon concentration in the seawater, as well as the lipid content of the oyster, apparently affects the rate and extent of accumulation. The oysters having a higher lipid content accumulated more hydrocarbons. When oysters were transferred to uncontaminated seawater, there was a rapid discharge of about 90% of the hydrocarbons

taken in. However, the amount retained was over 30 times that found in the oysters prior to exposure to the hydrocarbons. The hydrocarbons discharged by the oysters were greater in aromatic content and seemed to be somewhat degraded relative to the hydrocarbons present at the time of exposure; this prompted Stegeman and Teal to suggest the possibility that oysters modify the hydrocarbons.

Accumulation in Sediments

Shelton and Hunter (41) document the existence of hydrocarbons in bottom sediments. They cite the American Petroleum Institute's estimate of the national pollution potential from oil as about 450 million gallons annually, some of which reaches aquatic environments. Shelton and Hunter state that a significant portion of the aquatic input is incorporated into bottom sediments of receiving waters. Much of the PAH found in bottom sediments may be the result of natural forest and prairie fires. The PAH, while adsorbed on particles or in solution, may eventually reach the beds of the various water bodies and be taken up by bottom organisms or, in the absence of light and under anaerobic conditions, remain in a stable condition for long periods (13). Additional discussion of hydrocarbons in sediments is presented in the following sections.

Solubility

The fate of hydrocarbons in natural water systems is influenced by their solubilities. The solubility of a hydrocarbon determines whether it will go into solution, become suspended in the water column, or adsorb onto the sediments.

In discussing hydrocarbon solubility, it is important to consider the possible incorporation of hydrocarbons into micelles, a process thought to be responsible for some hydrocarbon solubilization in natural systems (42)(43). A micelle is composed of an aggregate of single-surface-active molecules (surfactants), each possessing a hydrophobic hydrocarbon chain and an ionizable or water-soluble group, hydrophilic in nature (e.g., sodium lauryl sulfate) (42):

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2-SO_4^- Na^+$$

Hydrophobic   Hydrophilic

The solubilization of a hydrocarbon is thought to occur by association of the hydrocarbon (1) with the hydrocarbon core of a micelle, (2) with the polar surface of a micelle, or (3) with both the interior and the surface; a hydrocarbon having low solubility in pure water (e.g., decane) can be incorporated into the micellar structure and become solubilized.

Boehm and Quinn (43) list the following natural sources for surfactant humic materials in seawater:

(1). Dissolved organic matter in seawater;

(2) Fulvic acid extracted from a marine sediment;

(3) Organic matter extracted by seawater from a marine sediment;

(4) Material isolated from seawater at a chloroform-seawater interface; and

(5) Organic matter contributed by a municipal sewage effluent.

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Removal of this dissolved organic matter from natural samples resulted in a 50 to 99% decrease in the amounts of hydrocarbons (primarily n-alkanes) solubilized. Solubilities of phenanthrene and anthracene were unaffected by the removal. However, high concentrations of surfactants (10 to 50 mg/ℓ) can increase the solubility of BP by a factor of 2 to 10 (44).

Another source of surfactants is microbiological. Microorganisms are thought to produce surfactants as metabolites to solubilize hydrocarbon droplets prior to assimilation (45)(46).

McAuliffe (47) has performed extensive determinations of the solubility of hydrocarbons. His studies indicate that branching increases the solubility of paraffin, olefin, and acetylene hydrocarbons, but not of cycloparaffin, cycloolefin, and aromatic hydrocarbons. For each homologous series of hydrocarbons, the logarithm of the solubility in water was found to be a linear function of the hydrocarbon molar volume. McAuliffe determined his solubilities in distilled water with measurements by a gas-liquid partition chromatographic technique. The chromatograph indicated slight impurity peaks, but McAuliffe assumed that these impurities did not interact with the hydrocarbon to alter the solubility.

Solubility of PAH in natural water systems seems to be poorly defined. Boehm and Quinn (43) report the PAH, phenanthrene, to be quite water-soluble. Three concentrations of phenanthrene (1.0, 0.5, and 0.1 mg/100 ml) added to Narragansett Bay water yielded solubility values of 60 to 70 μg/100 ml for all three concentrations. In two samples of Providence River water, Boehm and Quinn found phenanthrene solubilities of 24.6 and 15.5 μg/100 ml. The authors give no explanation for the higher solubility of phenanthrene in Narragansett Bay water than in Providence River water. They define soluble hydrocarbons as those hydrocarbons passing a 0.5-μm filter and solubilization as the process resulting in passage of the hydrocarbons by this filter. These researchers also found that neither salinity nor dissolved organic carbon had an effect on the solubility of phenanthrene, implying that phenanthrene is not solubilized by micelles.

McGinnes and Snoeyink (2) report that PAH are not soluble in water, but are present either as particulate material or as material adsorbed onto solid surfaces in natural water systems. Andelman and Suess (4) report that the solubility of PAH is very low in pure water, but that the increase of solubility of PAH by the addition of water-soluble organic compounds is a phenomenon that is important in the passage of these compounds into and through environmental waters. Thus, the solubilization of PAH is enhanced by the presence of micelles; this conclusion seems to contradict the results of Boehm and Quinn (43), who found dissolved organic carbon to have no influence on phenanthrene and anthracene solubility. However, since no two PAH compounds can be assumed to behave similarly with regard to solubility or any other property without sufficient experimental data, the results of Boehm and Quinn cannot definitely be reported as contradictory to the work of Andelman and Suess (4), who do not identify the specific PAH compounds about which they are writing. Grasselli (48) records phenanthrene as insoluble, but conditions for determination were not stated.

Clearly, the literature indicates that the solubilities of hydrocarbons, particularly PAH, in natural waters are poorly understood, presumably because of insufficient experimental data.

Degradation—Photooxidation

Photooxidation of hydrocarbons, particularly PAH, is the most important process in hydrocarbon degradation in air and water (13). Suess refers to results from his other published data and predicts that BP degradation in natural waters will be higher in the upper strata because the factors that promote degradation (illumination, temperature, and oxygen concentration) are high; degradation will decrease with depth due to a reduction in water clarity, illumination, temperature, and oxygen concentration. He also predicts that degradation by photooxidation of PAH in river, lake, and sea deposits will be minimal due to the lack of penetrating radiation and oxygen.

Feldman (49) found that toluene and related aromatics having side chains can be photooxidized in the presence of a variety of materials such as H_2O, H_2O_2, and H_2O + $FeCl_3$; tetrahydronaphthalene, for example, photooxidized in the presence of H_2O and O_2, gives polymeric materials. Feldman suggests that hydrocarbon photooxidation is a precursor to the formation of tar in marine waters.

McGinnes and Snoeyink (2) studied the photodecomposition of particulate PAH in water using benzpyrene (BP) and 1,2-benzanthracene (BA). The BP particles, 1.5 μm in diameter, irradiated for 4 days with ultraviolet light of varying intensities, decomposed (as shown in Figure 3.2) from 1 mg/ℓ to a nominal concentration of 0.3 to 0.45 mg/ℓ; 55 to 65% of the original BP in suspension was photodecomposed. The residual BP did not further decompose, regardless of the length of irradiation, because the decomposed outer layers (about 0.2 μm thick) functioned as a shield, protecting the inner BP from photodecomposition. This implies that a residual BP core will remain in natural systems for all photodecomposed BP particles having a diameter greater than 0.4 μm.

The primary BP photodecomposition products are identified as benzpyrene quinones, probably benzpyrene-6,12-quinone and benzpyrene-1,6-quinone:
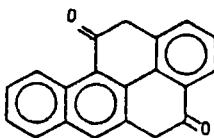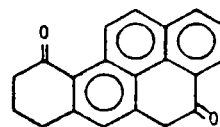
BP-1,6-Quinone   BP-6,12-Quinone

The decomposition products are unstable in the presence of ultraviolet light and are assumed by McGinnes and Snoeyink to decompose rapidly to secondary and tertiary decomposition products. McGinnes and Snoeyink (2) also irradiated BA particles having a diameter of 1.25 μm in a manner similar to that used for BP. Figure 3.3 shows that, in contrast to BP, BA continues to decompose with time. BA photocomposes to a benzanthracene-7,12-quinone:

BA-7,12-Quinone

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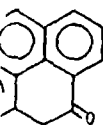
·Quinone

f ultraviolet light and
dly to secondary and
(2) also irradiated BA
to that used for BP.
decompose with time.

Figure 3.2: Decomposition of Particulate Suspensions of BP
Under Ultraviolet Light of Various Intensities

Source: Reference (2) as cited in ORNL/EIS-95

A secondary decomposition product is speculated. The BA photodecomposition
products were assumed to be either soluble in water or transparent to ultraviolet
radiation, thus explaining the complete decomposition of BA. Although these
are laboratory test results, the researchers feel confident that the results can be
extended to natural water systems.

The effect of particle size on decomposition of particulate PAH was also investi-
gated by McGinnes and Snoeyink. Samples were irradiated at an ultraviolet in-
tensity of 0.96 mW/cm²; BP samples underwent irradiation until a steady state
was reached while BA samples were irradiated for a 24-hour period. This investi-
gation showed an increase in percent decomposition for all samples when particle
size was decreased, thereby increasing total surface area available for photodecom·
position. This implies surface decomposition of both BA and BP.

Figure 3.3: Decomposition of Particulate Suspensions of BA
Under Ultraviolet Light of Various Intensities
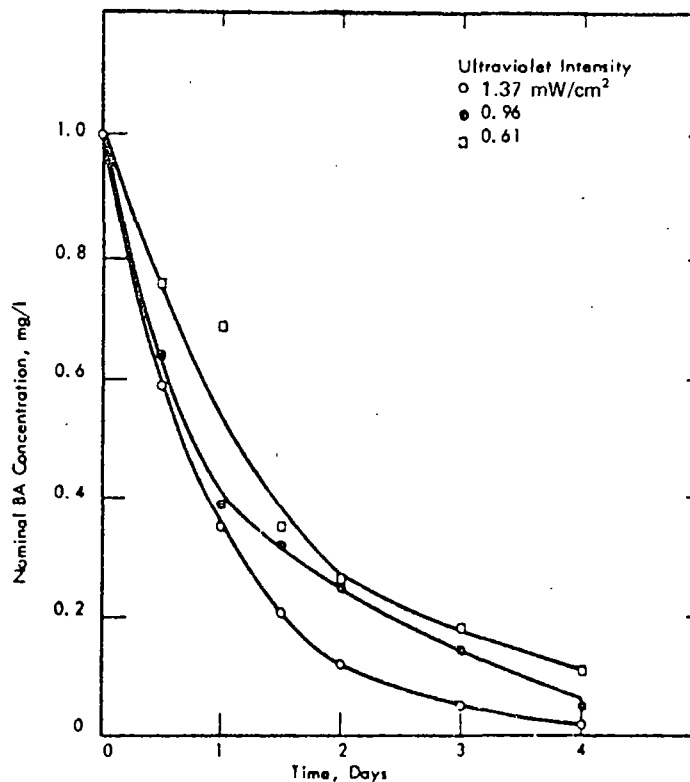
Source: Reference (2) as cited in ORNL/EIS-95

Freshwater Biodegradation

Several researchers have proposed biodegradation as a means for decomposition
of hydrocarbons in the environment. Feldman (49) states that the interactions
or pathways of such materials as trace or heavy metals, vitamins, amino acids,
EDTA, nutrient forms of phosphorus and nitrogen, DDT, and PCB influence the
biodegradation of hydrocarbons. These trace materials and compounds tend to
concentrate in the surface layer and can interfere with the succession of biota,
each of which uses a particular petroleum fraction, or an intermediate product.

Ludzack and Ettinger (50) measured the biodegradability of naphthalene, ethyl-
benzene, and Tetralin; the data were expressed in terms of the cumulative carbon
dioxide recovered as a percent of theoretical recovery vs time in days. Theoret-
ical carbon dioxide was obtained from the stoichiometric ratio of chemical to
carbon dioxide after complete oxidation. The results indicate that naphthalene,
Tetralin, and ethylbenzene were biodegraded at a moderate rate (more than 15

days for 50% CO_2 recovery); microbiological adaption to these compounds was poor.

Kostyaev (51) states that the activity of phenol-oxidizing bacteria, which exist in air, water, and soil, depends primarily on the temperature of the surrounding medium. He conducted experiments at 10°C and found that 5% of the original phenol decomposed, whereas at 30°C, 65% of the original phenol decomposed. Jeffery (52) found that the rate of phenol oxidation in his studies increased with increased air flow through the medium.

Marine Biodegradation

Suess (13) points out the existence of some controversy concerning the ability of marine organisms to degrade PAH. He cites the works of Reichart et al (1971) and Malaney et al (1968) as two examples of biological treatment processes having little or no efficiency in removing PAH and the work of Poglazova et al (1972) as an example of successful degradation of PAH by a mixed microbial culture. According to an NAS report (29),

> Microorganisms capable of oxidizing constituents under the right conditions have been found in virtually all parts of the marine environment that have been examined.... Both laboratory experiments and some field observations have shown that microorganisms consume the least toxic fraction of petroleum (normal alkanes) in a few days or months, depending on temperature and nutrient supply.. The fraction containing aromatics and naphthenes is more toxic than the alkanes and also degrades more slowly.

The degradation of PAH may also be assisted by more highly developed aquatic fauna (13).

Sedimentary Biodegradation

A significant portion of the oil pollutants discharged into aquatic environments is incorporated into bottom sediments of receiving waters. Shelton and Hunter (41) cite Tauson (1934) in discussing one mechanism of the anaerobic decomposition of hydrocarbons in freshwater sediments. Tauson's calculations indicate that the lower-molecular-weight saturated hydrocarbons may be oxidized microbially to CO_2 and H_2O at the expense of sulfate oxygen, whereas higher members of the series, starting with nonane (C_9H_{20}), may be transformed into naphthenes and polynaphthenes that are of no use to sulfur-reducing bacteria due to the negative heat effect accompanying their oxidation with sulfate.

Shelton and Hunter (41) report that there will be a gradual loss of the low-boiling petroleum fractions and an accumulation of naphthenic and polynaphthenic acids in sediments if the transformation of oil under natural anaerobic conditions occurs as Tauson indicates. These acids can be expelled to the surface and completely oxidized if, for example, there is gas formation on a river bottom to act as a carrier.

Baker (53) suggests that the fate of hydrocarbons in marine sediments is to form crude oil. The oil-forming mechanism is as follows:

(1)   Recent sediments and crude oils contain some of the same kinds of hydrocarbons that appear to be derived from the organic compounds produced by living organisms.

(2) Because the majority of the hydrocarbons which may later become collected to form crude oil deposits appear to be present in the sediments relatively soon after decomposition, no geologic time factor seems to be involved in hydrocarbon formation.

(3) Formation waters may contain natural solubilizers, which would enhance the solubility of hydrocarbons. Such waters could selectively dissolve and release sediment hydrocarbons in proportions that correspond to hydrocarbon occurrence in crude oils.

(4) The solubilizing ability of the formation waters is thought to be sensitive to both salt concentration and dilution. Consequently, hydrocarbons could be abruptly released as the interstitial waters pass from shale to sand or as the micelles diffuse throughout the sand.

(5) The hydrocarbons that are released would appear for the first time as tiny oil droplets (oil shows). They could coalesce and collect in the highest parts of the reservoir rock to form regions of high oil saturation (oil pools). The principles involved here are the classical ones of buoyancy and capillary-pressure-entry-pressure mechanisms.

In summary, the ultimate fate of hydrocarbons in the water environment is (1) dispersal in the water column, (2) incorporation into sediments, or (3) oxidation by chemical or biological means to CO_2 (29).

FATE IN SOILS

Soils exhibit differences in pH, texture, structure, and chemical composition (54). Thus, movement of additives within the soils is affected by the interrelation of the macrofeatures (texture, structure, pore space, and density), the humic nature of the surface horizons, and the four components of soil (solid, liquid, gaseous, and living). The solid component has a surface microcharacter that adsorbs, reacts with, and catalyzes reactions of both added and indigenous substances. This microcharacter is generated by crystalline mineral colloids, amorphous mineral colloids, organic colloids, and their surface character. The soil liquid component has special acidity-alkalinity properties due to the variable salt solution concentration, which may be buffered and which change with changing soil moisture.

Since the water phase is strongly adsorbed, it competes for solid surfaces. The soil atmosphere (gaseous component) is a modification of normal air; microbial activity and limited rates of diffusion cause a lower oxygen content and a higher carbon dioxide content than in air. The living component is the most complex. Organisms introduce into the soil many enzymes capable of metabolizing both natural organic substances and synthetic organic additives.

Leaching

Contamination of groundwater by leaching of organic chemicals through soil is an environmental concern (55). The ability of a chemical to reach groundwater depends upon not only its movement through, but also its disappearance from,

the soil; that is, if the rate of degradation is sufficiently rapid, as compared with the rate of leaching, the chemical will disappear before it can reach the groundwater. Determination of soil leaching rates indicates how long a chemical is retained in the top soil, where it is most subject to degradation or dissipation. Four major elements of leaching (55) are:

(1) · Soil adsorption, which determines an underlying pattern;

(2) Porous flow and diffusion, which disperse the chemical;

(3) Adsorption dynamics, which introduce a factor of hysteresis; and

(4) Water infiltration and evaporation, which determine the actual amount of water movement and, hence, the observed amount of chemical movement.

Adsorption

Many different intermolecular interactions are involved in adsorption of organic chemicals such as PNA by soils (Table 3.19) (56). Clay minerals (mainly kaolinite and montmorillonite)), organic matter (humin, humic acids, and fulvic acids), and hydrated metal oxides (aluminum and iron oxides), the three major soil components for adsorption, can each contribute to or compete for the adsorption of a soil contaminant, depending on the interactions available to the system. Hamaker and Thompson (56) conclude that adsorption in soil is largely due to small molecules interacting with macromolecules such as the soil organic matter.

Table 3.19: Intermolecular Interactions

Type of Interaction	Forces Involved
Van der Waals-London	Electrostatic
Hydrophobic bonding	Entropy generation
Charge transfer	Electrostatic
Hydrogen bonding	Electrostatic
Ligand exchange	Electrostatic
Ion exchange	Electrostatic
Direct and induced ion-dipole and dipole-dipole forces	Electrostatic
Chemisorption	Electrostatic
Magnetic bonding	Magnetic

Source: Reference (56) as cited in ORNL/EIS-95

Baker and Luh (57) attribute pyridine sorption onto sodium kaolinite and sodium montmorillonite from aqueous solution to cationic exchange of pyridinium ions with sodium ions. The extent of sorption depends upon the pH of the solution. Maximum pyridine sorption for sodium kaolinite occurs at a pH of 5.5, and maximum pyridine sorption for sodium montmorillonite occurs at a pH of 4.0. Sorption does not occur if the pH is greater than 6.0.

Roberts, Street and White (58) describe the physical processes of phenol adsorption by amine-activated montmorillonite. Wetting with water usually results in a considerable basal spacing expansion, whereas the adsorption of the phenol causes a progressive contraction of the mineral lattice. Formation of a quater-

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nary ammonium chloride montmorillonite results in a much greater basal expansion and a correspondingly greater adsorption of phenol. The amount of phenol adsorbed increases as the number of milliequivalents of quaternary ammonium base in the clay increases.
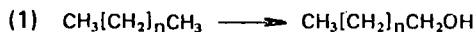
Porous Flow, Adsorption Dynamics, and Water Infiltration

A chemical flowing through a porous medium is either dispersed or retarded, depending on the porosity of the medium (55). This is a dynamic effect, which depends upon the movement of the liquid through pores. Diffusion allows the chemical to flow into stagnant pores to be released slowly when the main body of chemical has passed. A frictional effect caused by adsorption results in slow release of a chemical as soil readjustment takes place.

The pattern of rainfall and evapotranspiration determines the infiltration and movement of water into and through soil. Chemicals are leached downward following a rain, but as evaporation dries out the upper layers of soil, there is a compensating upward movement of water and chemicals. Letey and Oddson (59) observed that energy from the sun causes evaporation at a soil surface, resulting in the soil becoming drier; consequently, soil suction increases and a hydraulic gradient causes upward water flow, which could transport organic chemicals back to the surface. Hamaker (55) concludes, on the basis of published information, that little, if any, organic chemical ever leaches to groundwater.

Decomposition

The decomposition of hydrocarbons by soil microorganisms is the most important process in hydrocarbon degradation. Meikle (60) discusses the decomposition of saturated, unsaturated, alicyclic aliphatic, and aromatic hydrocarbons. Saturated aliphatic hydrocarbons undergo three types of reaction in soil and in cultures of microorganisms: oxidation of the terminal carbon atom, oxidation of the C_2-carbon atom, and dehydrogenation:

(1) $CH_3[CH_2]_nCH_3 \longrightarrow CH_3[CH_2]_nCH_2OH$

(2) $CH_3[CH_2]_nCH_2CH_3 \longrightarrow CH_3[CH_2]_n\overset{\displaystyle OH}{\overset{|}{C}}HCH_3$

(3) $CH_3[CH_2]_nCH_2CH_2[CH_2]_mCH_3 \longrightarrow CH_3[CH_2]_nCH=CH[CH_2]_mCH_3$
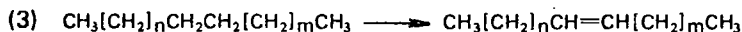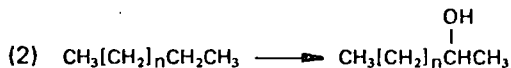
According to Meikle, the predominant soil reaction is Reaction (1). However, the usual isolated product of the microbiological oxidation of saturated aliphatic hydrocarbon chains is a carboxylic acid (Stewart et al 1959, as cited by Meikle) or glycolipid (Jones and Howe 1968; Makula and Finnerty 1968, as cited by Meikle) rather than the hydroxyl compound implied in Reaction (1). Alcohols are thought to be the intermediates in the sequence that produces the carboxylic acid. Meikle believes Reaction (2) to be of relatively minor importance in the oxidation of saturated aliphatics. As evidence of Reaction (3), Meikle cites the work of Tamura and Manire (1968), in which hexadecane was converted to a mixture of internal monohexadecanes.

Microbial decomposition of alicyclic aliphatic hydrocarbons is discussed by Meikle (60). Reaction (4) illustrates the hydroxylation of an unactivated methylene group, and Reaction (5) shows a steroid aromatization reaction.

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Microbiological degradation of the aromatic nucleus is accomplished with relative ease, resulting in destruction of the ring and leading to the ultimate use of the fragments by microorganisms as a source of carbon for growth.

Fernley and Evans (61) and Davies and Evans (62) both present the degradative pathways of the PAH naphthalene by soil pseudomonads (Figure 3.4 through Figure 3.6). Both groups of researchers agree that naphthalene is oxidatively metabolized by soil pseudomonads through D-trans-1,2-dihydroxynaphthalene to 1,2-dihydroxynaphthalene, which then undergoes ring cleavage. At this point, however, disagreement arises. Fernley and Evans say that the ring fission product is o-carboxy-cis-cinnamic acid (Figure 3.4), whereas Davies and Evans believe that the ring fission product is cis-o-hydroxybenzalpyruvate, isolated as the crystalline perchlorate (Figure 3.6). The two groups of researchers do agree that naphthalene is completely dissimilated by soil pseudomonads.

Phenanthrene and anthracene can be completely dissimilated by soil pseudomonads (63) (Figure 3.7). As with naphthalene metabolism, the ring fission mechanism with ring cleavage occurs at the 3,4-dihydroxyphenanthrene (Figure 3.7). The final metabolism is accomplished through the naphthalene pathway (Figure 3.6). Anthracene metabolism by ring fission (Figure 3.8) is similar to that for phenanthrene, although the final metabolism is conducted by unknown pathways. Evans, Fernley and Griffiths (63) state that PAH, occurring as various derivatives, can be completely dissimilated by soil pseudomonads.

Muller and Korte (64) studied the microbial degradation of BaP. The chemical was sprayed on ground waste, and after three weeks of composting, the digested material was extracted by organic solvents. They found that BaP withstood degradation by at least 99.5%; however, the researchers indicate that Lorbacher, Püls, and Schlipköter (1971) found that BaP can be accumulated and converted by special strains of microorganisms.

Hussien, Tewfik and Hamdi (65) demonstrated the ability of 22 strains of *Rhizobium* to degrade the aromatic compounds, catechol, protocatechuic acid, p-hydroxybenzoic acid, and salicylic acid. At 1 mM concentration and in the presence of 4.8 mM sodium glutamate, all rhizobia tested degraded catechol (99 to 100%), p-hydroxybenzoic acid (79 to 99%), protocatechuic acid (81 to 97%), and salicylic acid (20 to 83%). Increased glutamate concentration favored degradation of p-hydroxybenzoic and salicylic acids, had little observable effect on catechol, and inhibited the degradation of protocatechuic acid. The researchers

found that most strains of rhizobia tested readily used catechol and protocate-chuic acid without detectable accumulation of intermediate phenolic compounds, but p-hydroxybenzoic acid apparently was converted to protocatechuic acid before ring cleavage. Also, they found salicylic acid to be slowly degraded by different strains of rhizobia in liquid cultures, being first converted to another compound identified as gentisic acid.

An understanding of simultaneous leaching and degradation is needed to properly understand the movement of chemicals through the soil and into the groundwater (55).

Figure 3.4: Suggested Pathway for the End-Ring Attack on Naphthalene by Soil Pseudomonads
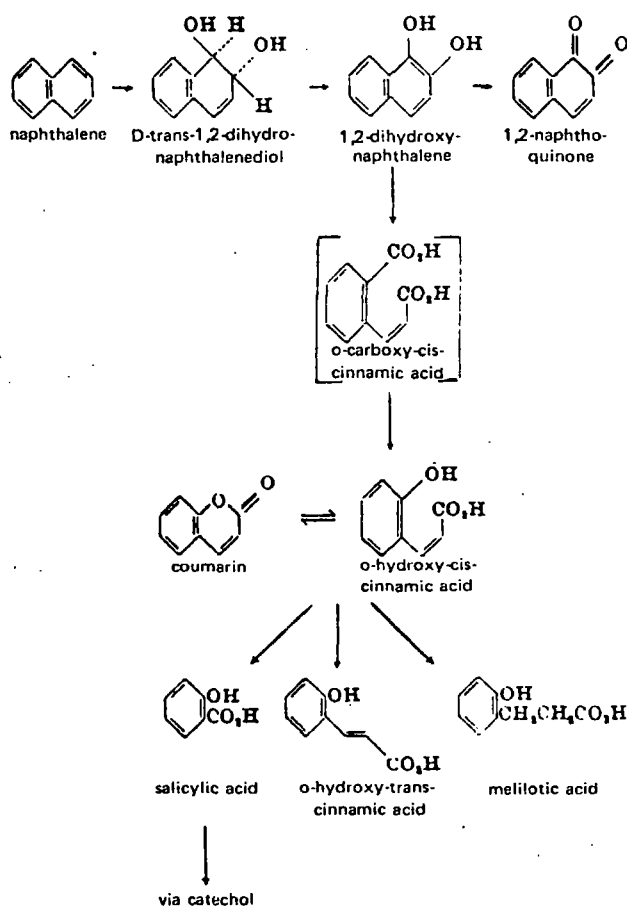
Source: Reference (61) as cited in ORNL/EIS-95

Figure 3.5: Possible Transformations of cis-o-Hydroxybenzalpyruvate

hemiacetal form   yellow anionic form   trans-yellow anion   trans-o-hydroxy-benzalpyruvate
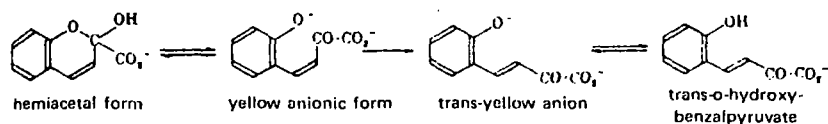
Source: Reference (62) as cited in ORNL/EIS-95

Figure 3.6: Proposed Pathway of Naphthalene Metabolism
by Soil Pseudomonads

naphthalene   D-trans-1,2-dihydro-1,2-dihydroxynaphthalene   1,2-dihydroxy-naphthalene   1,2-naphthoquinone

quinonoid structure of cis-o-hydroxybenzalpyruvic acid

2-carboxybenzopyrillium perchlorate   hemiacetal form of cis-o-hydroxybenzal-pyruvic acid   yellow anionic form of cis-o-hydroxybenzal-pyruvic acid   coumarin

α-hydroxymuconic semialdehyde   catechol   salicylate   salicyl-aldehyde   δ-hydroxy-δ-o-hydroxyphenyl-α-oxobutyrate

Source: Reference (62) as cited in ORNL/EIS-95

Figure 3.7: Proposed Pathway of Phenanthrene Metabolism
by Soil Pseudomonads
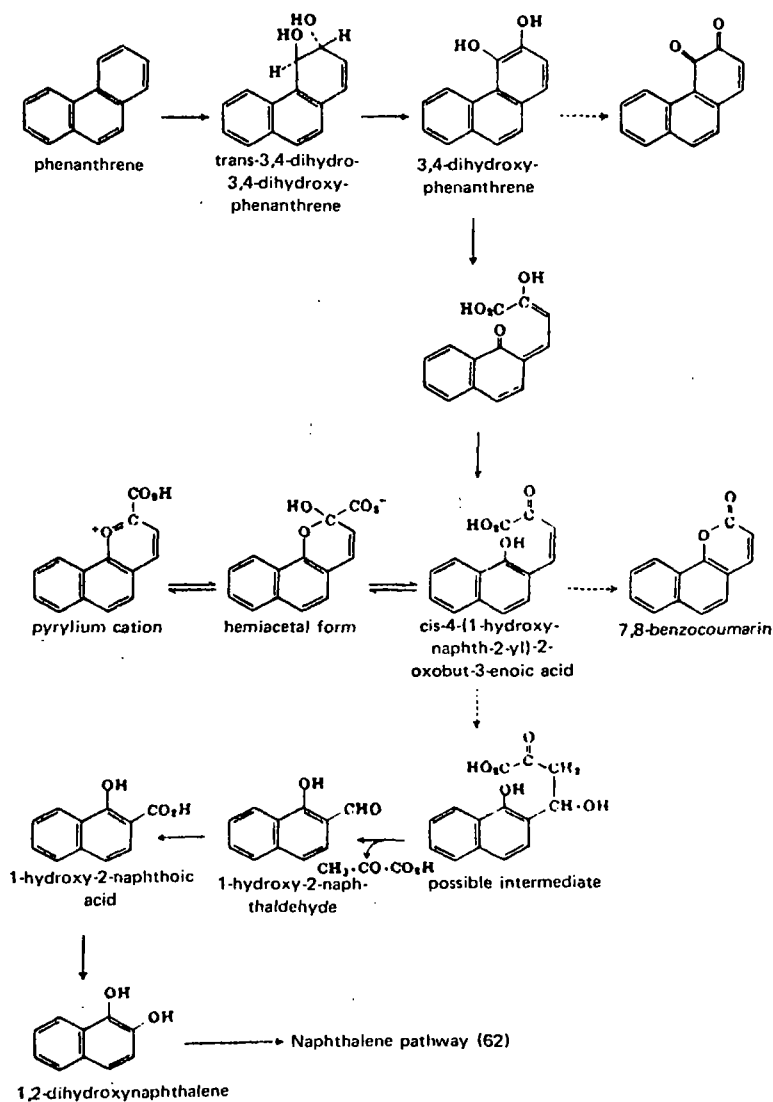
Source: Reference (63) as cited in ORNL/EIS-95

**Figure 3.8: Proposed Pathway of Anthracene Metabolism
by Soil Pseudomonads**

anthracene   trans-1,2-dihydro-1,2-
dihydroxyanthracene   1,2-dihydroxyanthracene

pyrylium cation   hemiacetal form   cis-4-(2-hydroxynaphth-
3-yl)-2-oxobut-3-enoic acid   6,7-benzocoumarin

2-hydroxy-3-naphthoic
acid   2-hydroxy-3-naphth-
aldehyde $CH_3 \cdot CO \cdot CO_2H$

2,3-dihydroxynaphthalene   ——▸ Unknown pathway through salicylate

7,8-benzocoumarin
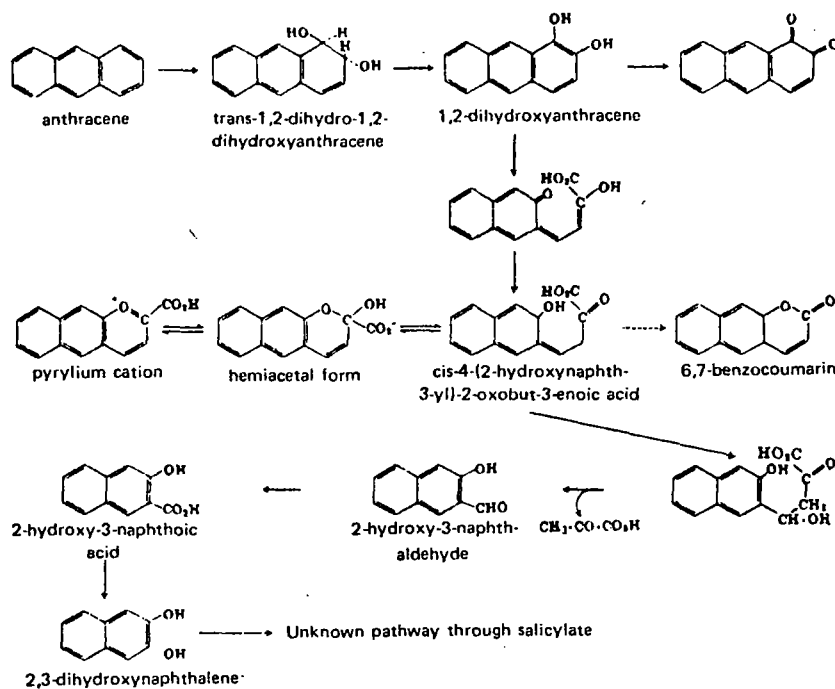
Source: Reference (63) as cited in ORNL/EIS-95

FATE IN AIR

In the atmosphere, polycyclic organic matter is associated with particulate matter, especially soot. Figure 3.9 illustrates some carcinogenic polycyclics that have been identified in urban air.

Collection of PAH on particulate filters is the method generally employed during air pollution surveys. Pupp et al (66) report that the volatility of some PAH compounds hindered their collection on particulate filters; losses occurred from the filter surface. The PAH compounds, pyrene and BaP, which have equilibrium vapor concentrations of 500 $\mu g/10^{-3}$ m^{-3} or higher at ambient temperatures, were reported to have considerable losses from filters during air sampling. These losses (plus losses by sublimation) and the fact, reported by Thomas, Mukai, and Tebbens (67), that not all PAH are absorbed even in the presence of excess soot led Pupp et al to question the accuracy of present collection methods. If the present collection methods are not totally representative of ambient PAH concentrations, then the discrepancy would most likely be in such a direction that the reported PAH atmospheric concentrations would be lower than the true value due to losses and unmeasured PAH.

Figure 3.9: Carcinogenic Polycyclics Identified in Urban Air

Chrysene

Benz(a)anthracene
(1, 2-benzanthracene)

Indeno(1, 2, 3-cd)pyrene
(o-phenylenepyrene)

Benzo(e)pyrene
(1, 2-benzopyrene)

Benzo(a)pyrene
(3, 4-benzopyrene)

Dibenzo(a, i)pyrene
(3, 4, 9, 10-dibenzopyrene)

Benz(e)acephenanthrylene
(3, 4-benzofluoranthene)

Benzo(j)fluoranthene
(10, 11-benzofluoranthene)

Dibenz(a, h)acridine
(1, 2, 5, 6-dibenzacridine)

Dibenzo(e, l)pyrene
(1, 2, 3, 4-dibenzopyrene)

Dibenzo(a, h)pyrene
(3, 4, 8, 9-dibenzopyrene)

Dibenz(a, i)acridine
(1, 2, 7, 8-dibenzacridine)

Source: Reference (26) as cited in ORNL/EIS-95

Physical Reactivity

Particle size is the physical property having the greatest influence on the bioenvironmental behavior of aerosols containing polycyclic organic matter (3). A seasonal study of PAH association with particulate matter found that most PAH were associated with particles less than 3.0 μm in diameter (68). During the summer months, 6 to 23% of the total atmospheric PAH were associated with particles having diameters ≤ 1.0 μm, whereas particles having a diameter ≤ 3.0 μm contained 56 to 70% of the total PAH content. During the colder winter months (this study was conducted in Toronto), the PAH content of the smaller respirable particles (< 1.0 μm) increased.

Pierce and Katz (68) note that particles having a diameter ≤ 5.0 μm are in the respirable size range, that is, the size range most likely to be deposited in the pulmonary portion of the respiratory tract. Figure 3.10 shows that 60% of all particulate matter in the size range of 0.5 to 2.0 μm that is inhaled is retained in the lung. The highest retention, 77%, occurs at 1.0 μm. DeMaio and Corn (69) found that aerosol particles < 5.0 μm in diameter contained more than 75% of the weight of selected polycyclic hydrocarbons.
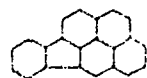
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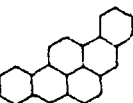
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, 4, 9, 10-dibenzopyrene)
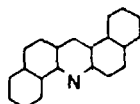
ibenz(a, h)acridine
1, 2, 5, 6-dibenzacridine)

Dibenz(a, i)acridine
(1, 2, 7, 8-dibenzacridine)

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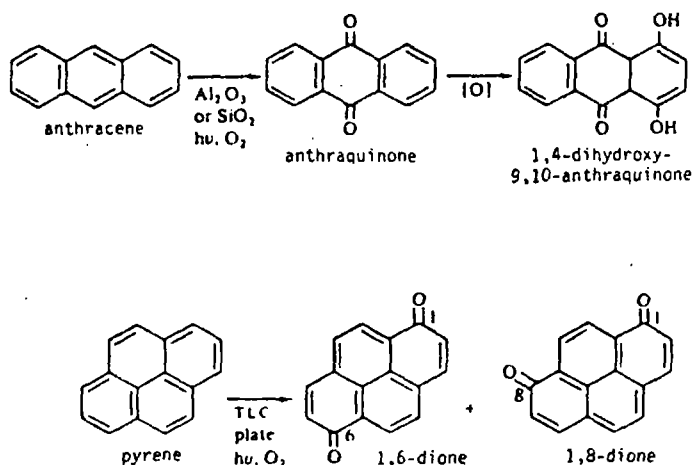shows that 60% of all
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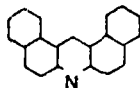
Figure 3.10: Retention of Particulate Matter in Lung
in Relation to Particle Size
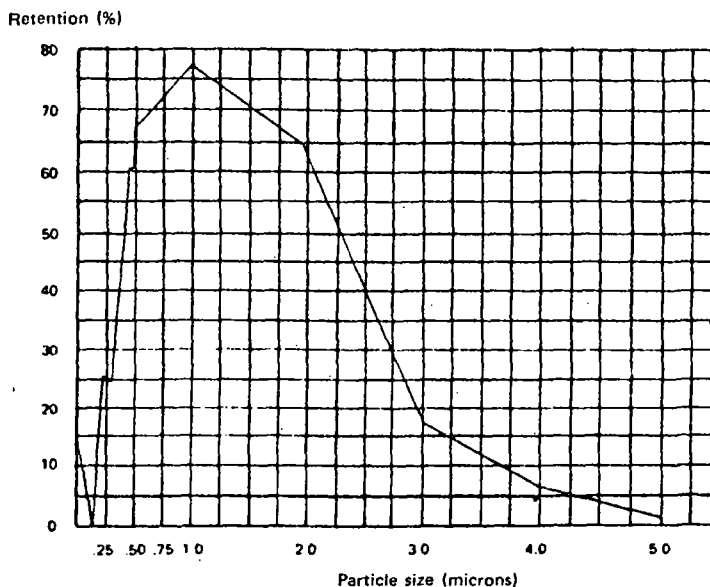
Source: Reference (26) as cited in ORNL/EIS-95

Atmospheric suspended particles evolve by the following mechanisms (3):

(1)   Growth or change in particles by homogeneous or heterogene-
ous chemical reactions of gases on the surface of particles;

(2)   Change in particles by attachment and adsorption of trace
gases and vapors to aerosol particles;

(3)   Net change by collision between particles undergoing
Brownian motion or differential gravitational settling;

(4)   Net change by collision between particles in the presence of
turbulence in the suspending gases;

(5)   Gain or loss in concentration by diffusion or convection from
neighboring air volumes;

(6)   Loss by gravitational settling;

(7)   Removal at the earth's surface on obstacles by impaction, in-
terception, Brownian motion, and turbulent diffusion;

(8)   Loss or modification by rainout within clouds; and

(9)   Loss by washout below cloud level.

These mechanisms can influence aerosol chemical composition, as a function of
size, and can affect the observed size distribution of aerosols.

The NAS report states that the lifetime of polycyclic organic matter in air depends on the carrier aerosol and on the chemical alteration of the matter itself. In dry atmospheric conditions, residence times of particles <5 μm in diameter exceed 100 hr, but in the presence of sunlight, chemical reactivity may lead to transition of polycyclic organic matter adsorbed on soot to other material in several hours.

Chemical Reactivity

The major mode of polynuclear compound removal from the atmosphere is through chemical reactions; for example, photooxidation is probably one of the most important processes in atmospheric removal of PAH (3). Thomas, Mukai and Tebbens (67) indicate that BaP and other arenes are primarily adsorbed on the surface of soot through hydrogen bonding. Chemisorption is apparently not feasible because of the rapid rate of photomodification, indicating that BaP must be primarily in an exposed position on the surface.

Tebbens, Thomas and Mukai (70) demonstrated a 15 to 50% loss of BaP in smoke on filters with 6 hr of sunlight exposure. Another study (71) shows a 10% destruction of BaP adsorbed on soot or a filter after a 48-hr exposure to light of unstated intensity and a 50% destruction after a 1-hr exposure to light and synthetic smog.

Products of photooxidation of adsorbed aromatic hydrocarbons (anthracene and pyrene adsorbed on silica gel and alumina) are given in the NAS report (3):

anthracene   Al₂O₃ or SiO₂ hv, O₂   anthraquinone   [O]   1,4-dihydroxy-9,10-anthraquinone

pyrene   TLC plate hv. O₂   1,6-dione   +   1,8-dione

The oxidation of both anthracene and pyrene took place in the presence of ultraviolet light and oxygen, the degree of anthracene oxidation being somewhat dependent on the adsorbent. The pyrene oxidation was conducted on thin-layer chromatography plates.

PAH also react with ozone, peroxides, nitrogen oxides, and sulfur oxides and undergo one-electron oxidation (3). They react with ozone in one of four ways:

(1) Cleavage of phenanthrene-like double bonds, which results in diacid formation under oxidative conditions;

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which results in

(2) Oxidation at anthracene-9,10-like positions to yield quinones;

(3) A more complex nuclear oxidation; and

(4) A side-chain oxidation.

A typical example is the ozonolysis of benz[a]anthracene, which undergoes cleavage of the phenanthrene-like double bond to yield a cleavage product, a quinone, and a phthalic acid:
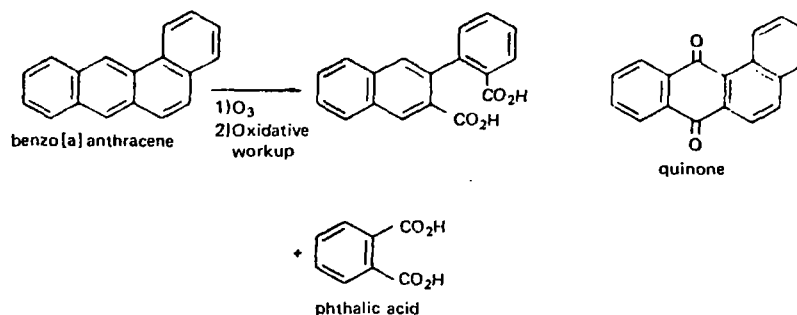
The peroxide reaction involves the interaction of benzoyl peroxide $[(C_6H_5CO_2)_2]$ with the PAH, in this case BaP, to yield the 6-benzoyloxy derivative:
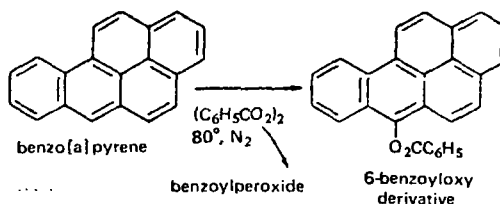
In the presence of oxygen, this peroxide reaction could lead to further oxidation. Nitrogen oxides or dilute aqueous HNO_3 oxidizes anthracene to anthraquinone:
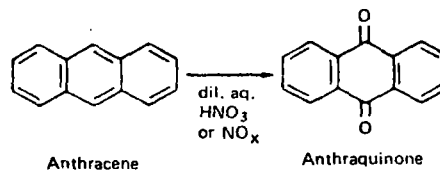
Specifically, the addition and substitution of NO_2 in anthracene yields an oxidation product by loss of HNO_2 from the intermediate compound:
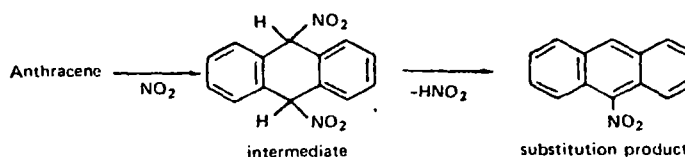
The one-electron oxidation of PAH results in the formation of radical cations as primary products; these react rapidly with water or other nucleophiles or with oxygen. The complete reaction leads to formation of quinones (with water and oxygen), nucleophile adducts, or dimeric hydrocarbons. One-electron oxidation of BaP also illustrates the formation of quinones:

Benzo[a] pyrene   Radical cation   1,6-Dione and
                                                  other quinones

Dimer
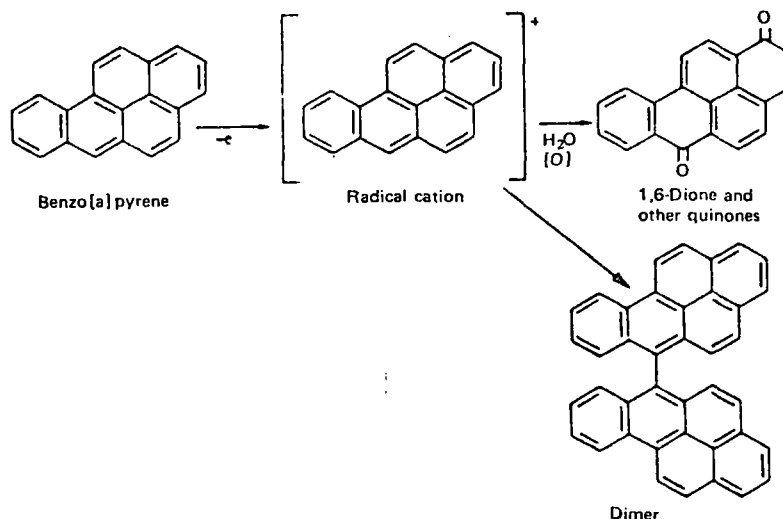
PAH also react with sulfur oxides, yielding sulfuric and sulfonic acids as products; these sulfur compounds will no longer appear in the benzene-soluble fraction because they are water-soluble.

ENVIRONMENTAL TRANSPORT SUMMARY

The environmental transport of hydrocarbons is summarized by Suess (13):

> ...the transport pattern of PAH in the environment appears to be relatively simple. The background PAH, which are formed by biosynthesis, are quite static and, obviously, remain in the plants and microorganisms in which they were formed and, more generally seen, stay within their own eco-systems. However, it appears probable that PAH in ground-water are leached out from the soil.
>
> In contrast, PAH formed by high temperature processes, whether resulting from natural open burning and volcanic eruptions or from man-induced combustion reactions, are all emitted into the atmosphere, and thus are subject to the same dynamic forces which govern the movement, transport and fallout of aerosols generally. Because a significant portion of PAH, adsorbed onto the aerosols, will decompose by photooxidation while still in the atmosphere, either stationary or in motion, their fallout at greater distances from the source (delayed fallout) will be relatively very limited. However, where fallout of PAH occurs, it will contaminate the upper layers of the earth, including vegetation and forests, as well as rivers, reservoirs and lakes, and some of them will also reach the oceans. Runoff and the rivers will carry eventually some of this fallout to the open seas and oceans. As waste treatment plants do not remove all PAH, the coastal

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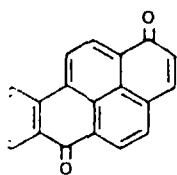
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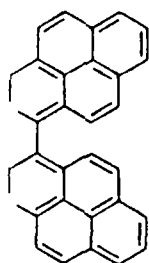
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effluents either directly, or indirectly through the rivers....

The degradation of PAH in the atmosphere by photooxidation will also
continue to some extent when they have settled back on earth and water
surfaces, for as long as they are exposed to sunlight. However, some PAH
will be degraded by soil bacteria and aquatic organisms. PAH, while ad-
sorbed on particles or in solution, may eventually reach the bed of the
various water bodies and be taken up by bottom organisms, or remain
there stable for extremely long periods, given absence of light and anaero-
bic conditions.

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